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*Analysis of the Hardening Reaction of Furfurylalcohol Resin**

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(Received January 13, 1958)

Measurement of electric resistivity of thermosetting resins during their hardening stage along with the several other methods[1] provides information on their curing degree. The methods, however, can be done only with difficulty with the common instruments readily at hand, because of the higher resistance value of resins.

In the earlier part of the resinification, mechanism of the accelerator's** action, unobtainable by chemical analysis[2], was easily pictured by this method[3], since the accelerator reduced the resistance of the reactant.

Addition of electro-conductive filler, which may similarly reduce the resistance, was considered to clarify almost the whole curing degree by employing common instruments. In this article, graphite powder was added to furfurylalcohol(FA) resin—one of graphite-cement systems—and Kohlrausch bridge-and drop-method were employed, which exhibited the activation energy of the final cure together with that of the apparent cure.

Experimental

Materials.—Resin—A neutralized initial condensate of FA. Viscosity—31.3 poise at 20°C. Mean Mol. Wt.—220 (Calculated from the freezing point depression of its dioxane solutions.)

Filler—Artificial graphite powder as shown in Table I.

Accelerator—*p*-Toluenesulfonyl chloride (I) and its sulfonic acid (II), reagents of G. R. Grade.

Solvent—Dioxane (G. R. Grade) was used only when the filler was not added, in order to keep the reaction temperature constant.

Mixture of filler and accelerator—One hundred g. of I or 30.0 g. of II was mixed with 1000 g. of filler for more than 45 min. in a mixer at room temperature.

TABLE I

CHARACTERISTICS OF GRAPHITE POWDER

Moisture		0.25%
Volatile Matter		0.84%
Ash		0.09%
Density d_4^{20}		2.073
Distribution of Particle size	<80 meshes	0%
	80～120	1%
	120～160	19%
	160～200	22%
	200～250	3%
	>250	55%

Method.—*1. Determination of resistivity (ρ_d, ρ_a) and apparent resistance (R).* (1) In the case where copper electrode was employed: more than 20 of the similar electrodes $5\phi \times 100$ mm. copper, which were polished prior to use, held by the epoxy resin plate* at intervals of 14.0 mm. were set in equal depths of the cement. Seventy g. of the resin and the same amount of filler containing I or II were mixed in a tall beaker ($45\phi \times 85$ mm., for 100 cc.) for 5 min. A thermometer was inserted in the center of the reactant. The beaker was placed in a thermostat. The plate*, connecting electrodes, was sealed to the beaker with hard clay. Apparent resistance (R) was measured by Kohlrausch bridge from the beginning of resinification to the final cure.

When the filler was not used, solutions containing 1.0 g. of I or 0.2 g. of II as well as 7.0 g. of dioxane and 30.0 g. of resin were prepared, R of which was determined uniformly by Wheatstone bridge instead of Kohlrausch bridge.

Hereafter, experiments, where I is used, will be called A-series and those with II, B-series.

(2) After gel-time the resin (130 g.) and the same amount of the filler containing I or II were mixed and hardened in the beaker, exactly parallel with the above mentioned system. Samples immediately after gel-time were rapidly cut out in approximate sizes $10 \times 10 \times 20$ mm., which were closely held between copper films and their resistivity was measured by the drop method (D. C. employed), and further by Kohlrausch bridge. These will be called ρ_d and ρ_a, respectively.

2. Measurement of adhesion power (F). At the same time that the graphite cement was prepared as mentioned, above "impervious

* Presented at the 10th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1957.

** *p*-Toluenesulfonyl chloride, which may react with the monomer or the initial condensate of the resin[3].

1) E. Barr, *Ind. Eng. Chem.*, **48**, 72 (1956).
2) S. Yamada and S. Hayashi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **61**, 342 (1958).
3) S. Yamada, This Bulletin, **27**, 479 (1954).

* Araldite D, cured with accelerator No. 951, resistance of which was infinitive between electrodes by 500 V. megger.

graphite"* pieces, cut out as large as 10×10×20 mm., were joined with the cement at the 10×10 plane under the same pressure. They were settled in the thermostat, being placed in a glass vessel with a stopper.

Adhesion power (F) was measured as the transverse strength at the joined plane, several values of which were averaged every time.

3. Acetone extraction. At the same time, when samples for measuring ρ_d and ρ_a were taken off, small cubes (10×10×10 mm. in size) were cut out at every curing temperature. Three pieces were held in the thermostat (30±0.1°C) with 25.0 cc. of acetone and weighed after 16 hr.

4. Other measurements.—Shrinkage** of samples employed for the determination of resistivity, filler added, was measured with a micrometer, which gave an exactness of 0.2% to the completely cured cement pieces.

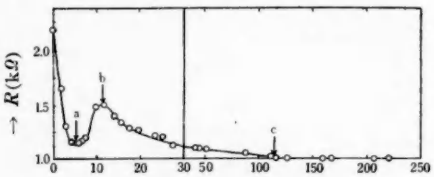

Fig. 1. An example of change in apparent resistance, filler employed.

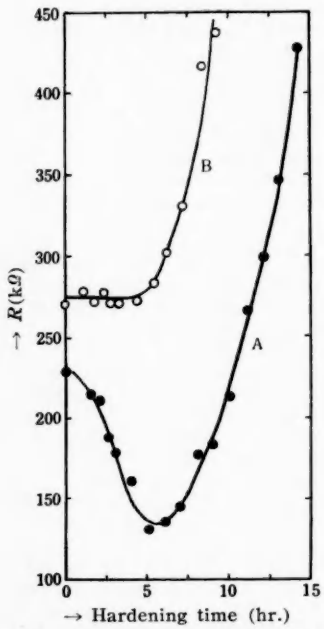

Fig. 2. An example of change in apparent resistance (R), without filler at the earlier stage.

* "Impervious graphite" is made by impregnating a thermosetting resin.

Hardness** was measured with Shore tester complementally.

5. Hardening temperature. 20, 30, 40 and 50, ±1°C were adopted.

Examples of data.—*1. Change in apparent resistance, R.* For instance, data in the case of B-series with filler at 20°C are given in Fig. 1. Reproducibility of the point a, b and c was excellent. Change in R of the reactants without filler at 40°C is shown as an example in Figs. 2 and 3.

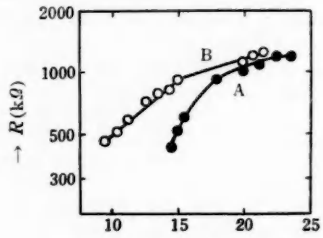

Fig. 3. An example of change in apparent resistance (R), without filler at the final stage.

2. Change in adhesion power, F and hardness H. Data at 30°C are given in Fig. 4 for example.

3. Change in resistivity, ρ_d, ρ_a. Data at 30°C are given in Fig. 5 for example.

4. Change in acetone extract. Data at 40°C are shown in Table II for example.

TABLE II

AN EXAMPLE OF CHANGE IN ACETONE EXTRACT

Series	Reaction time (hr.)	Average (%)	Range (%)
A	51	7.60	0.55
	75	1.73	0.05
	99	2.50	0.35
	118	2.74	0.08
B	51	5.60	1.40
	75	3.30	1.70
	99	1.35	0.02
	118	1.85	0.10

5. Change in shrinkage. Data at 50°C are shown as an example in Table III.

Discussion

1. Change in R, ρ_d and ρ_a.—Elements of change in R may be assumed as R_h, R_w, R_a and R_g. For example; $-dR_h/dt = K_h \cdot V_h$, $-dR_w/dt = K_w \cdot V_w$ etc. Increasing and decreasing velocity of R_h, R_w etc. may be considered to be proportional to that of hardening and dehydrating process.

** Samples were held in a glass vessel set in the thermostat, and at the stopper and the bottom of the vessel dry granules of calcium chloride were placed.

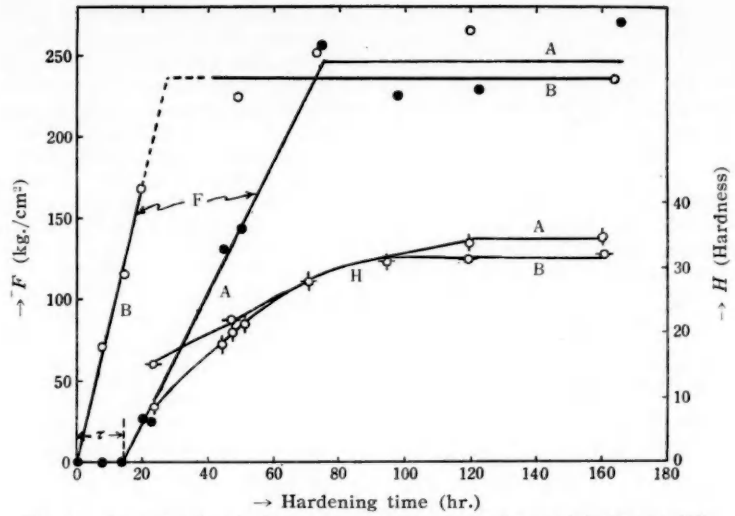

Fig. 4. An example of change in adhesion force (F) and hardness (H).

TABLE III

AN EXAMPLE OF CHANGE IN SHRINKAGE

Series	Reaction time (hr.)	10×10×20 mm.			10×10×10 mm.			10×10×10 mm.		
A	26	9.98	9.95	20.04	9.90	9.96	9.92	9.95	9.90	9.88
	50	−0.01	−0.03	−0.05	−0.01	−0.01	−0.03	−0.01	−0.01	−0.01
	74	〃	〃	〃	〃	−0.02	−0.02	−0.01	−0.02	−0.02
	94	0.00	−0.02	−0.04	0.00	〃	−0.03	0.00	0.00	0.00
B	26	9.91	9.91	20.02	9.93	9.99	9.95	9.99	9.91	9.91
	50	0.00	0.00	−0.02	−0.02	−0.01	−0.02	0.00	−0.01	−0.02
	74	−0.01	−0.01	−0.03	−0.03	−0.02	−0.03	−0.01	〃	−0.03
	94	〃	〃	−0.04	〃	−0.01	−0.04	〃	〃	−0.04

TABLE IV

COMPLEMENTARY DATA TO EXPLAIN THE SETTLING DOWN TENDENCY OF RESISTANCE

Particle size of graphite powder (meshes)	Molding pressure (kg./cm.²)	Comparison[a] between ρ_1, resistivity of sample immediately after molding and, ρ_2, that after curing up to 200°C	Resin
24—32	40	$\rho_1 > \rho_2$ (α=1%[b])	Initial condensate of FA[c]
32—50	〃	$\rho_1 = \rho_2$ (〃)	〃
50—80	〃	$\rho_1 < \rho_2$ (〃)	〃
50	100, 200, 300, 400, 500, 600.	$\rho_1 = \rho_2$ (〃)	Phenollic

a) Tested by analysis of variance in three-way layout.
b) Risk.
c) In the case where the ratios of the resin added to filler change, ρ_2 decreases to a ratio (12% to filler) and then increases starting from the ratio, as the amount of resin increases.

R_a and R_d correspond to the activation of I[3] and orientation of graphite filler respectively. Values of change in R, dR/dt may be plus, zero or minus depending on the value of each element. It is assumed that V_w and V_a contribute in the early stage and V_h and V_g in the final stage. Change in R, ρ_d, and ρ_a indicated in Figs. 1 and 5, for example, are observed to be of a settling down tendency in the final stage.

On the contrary, the system without

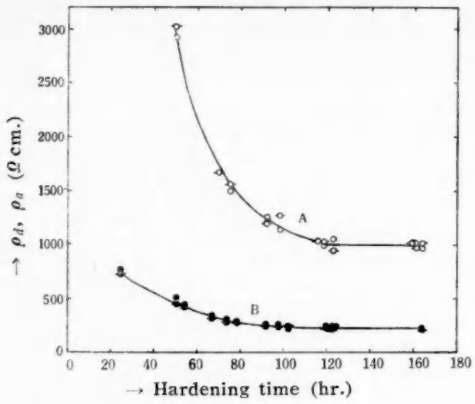

Fig. 5. An example of change in resistivity (ρ_d, ρ_a).
◇ ●: ρ_d } These can be considered to
○ ●: ρ_a } be in an approximate agreement.

graphite filler indicates a reasonable increasing tendency as shown in Fig. 3 for example. This fact amply suggests that the effect of filler, $-dR_g/dt$, governs the hardening degree in final stage. Experimental facts from another view as shown in Table IV give a hint to the phenomenon, which may be derived from the following interpretation.

Data in Table IV indicate that the effect of graphite powder on the resistivity directly relates to its particle size and molding pressure. In this article, meshes smaller than 120 of graphite powder and the normal pressure were employed. The facts given in Table IV are summarized as follows.

(a) In the case where coarse particles were used, resistivity decreases with hardening and increase in resin content under a relatively low pressure.

(b) In the case where particle size is reduced, resistivity does not change or increase under the pressure.

(c) In the case of use of fine particles, resistivity does not change under pressure.

Accordingly, the phenomenon of the decreasing tendency even in the case of fine particles used under the normal pressure in these experiments may not be contradictory to this fact. Namely, it is understood that the orientation time of the filler in the resin depends on the hardening velocity, amount and particle size of added filler, and the operating pressure.

From b to c in Fig. 1, the effect of the orientation is predominant, while the effect of hardening is observed from a to b.

Now that the settling time of resistivity can be assumed as the end point of hardening, its activation energy from this time, S_ρ, was calculated to 7 kcal./mol. in A-series*, 6 kcal./mol. in B-series as shown in Fig. 6. Such values can not be obtained from changes in acetone extract given in Table II. under similar conditions.

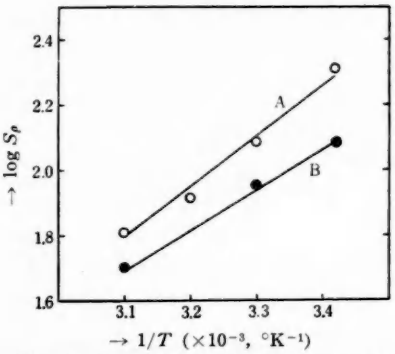

Fig. 6. Relation between log S_ρ and $1/T$.

Besides, the activation energy calculated from the time up to a certain R in Fig. 3 for example (no filler) was 12 kcal./mol.

Cell constant of the cell used, K=9 cm. was obtained by employing saturated aqueous solution of sodium chloride. The resistivity of the cut piece, ρ_a, was however found to be different from that calculated from R (with filler).

This proves that the mixing of resin and filler containing accelerator could not be uniformly processed even in such a small scale, which may be a point to take in consideration in applied use. Large variance in acetone extract as given in Table II may depend upon the same fact.

2. Change in adhesion power, F.—In A-series, the induction period τ for the increase of F was observed as shown for example in Fig. 4. This may be assumed to correspond with the activation velocity of I and gives activation energy of the process, 12 kcal./mol., as shown in Fig. 7.

Now further data in a previous paper[3] the relation between the decrease of the velocity of resistance in FA monomer and I, k_r—corresponds with the activation velocity of I—and the reaction temperature

* In A-series, accelerator concentration in the system is considered to increase because of formation of II and hydrochloric acid as I reacts with the resin[3]. Accordingly the energy is only an apparent value differing from that in B-series.

was investigated as shown in Fig. 8. which gave the activation energy, 10 kcal./mol. It may be considered to be closely related to the above value, 12 kcal./mol., in the case

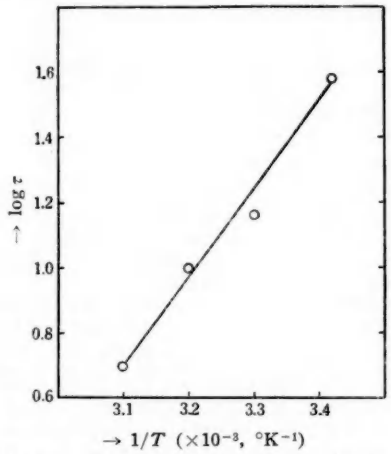

Fig. 7. Relation between $\log \tau$ and $1/T$.

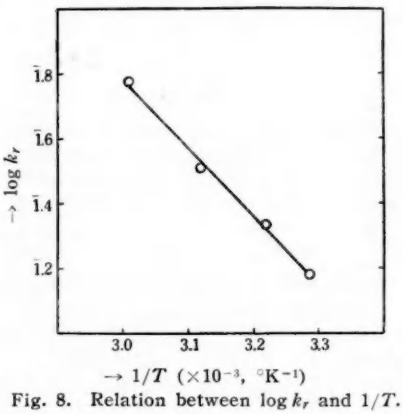

Fig. 8. Relation between $\log k_f$ and $1/T$.

where filler and initial condensate are employed. It is interesting that these values are relatively similar in spite of the difference both in the calculation method and of the reaction system.

Approximate saturation time of F, S_F, in B-series (catalyst concentration is constant), gave, as shown in Fig. 4, the activation energy, 16 kcal./mol., which may be assumed as that for the apparent end point of the hardening process. In this determination, saturated value of F was obtained by averaging arithmetically, such a variance which was inevitable in such a case and similar variances are noted in many reference papers[4].

3. Other problems. — The saturation time of H was greater than that of F in each case as given for example in Fig. 4, which suggests that the saturation time of the F above mentioned gives only an apparent end point of the hardening process.

Change in shrinkage was in the limit of experimental error in almost all cases, which may explain that the settling down phenomenon of resistivity does not depend on the apparent shrinkage.

Summary

Decreasing tendency of resistance in the system consisting of furfurylalcohol resin, graphite filler and accelerator was observed and analysed, and this observation gave an activation energy of the final cure, together with that of the apparent cure calculated from the saturation time of adhesion power. Besides, activation of sulfonylchloride accelerator was investigated taking account of the adhesion power increase and resistance decrease.

These considerations may be full of suggestions for the practical use of such a cement system.

The authors wish to express their thanks to Professor H. Sobue, of Tokyo University for his valuable suggestions, to Mr. G. Sakurai, factory chief of Tokai Electrode Mfg. Co., for his instructive advice and encouragement, and to the authorities of Tôkai Electrode Mfg. Co., for the publication of this article and also to Mr. S. Takata and Mr. H. Matsumoto for their assistance.

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4) e. g., E. O. Hausman, A. E. Parkinson and G. H. Mains, *Modern Plastics*, **22**, 151—154, 190—198 (1944).

Hydrothermal Treatment of Fluor-phlogopite.—Hydrothermal Treatment of Agglomerate Mass of Synthetic Mica Crystals to Facilitate Separation of Individual Crystals

By Tokiti NODA*, Hajime SAITO**, Isao TATE**, Tsutomu FUKASAWA**, Masahiko FUKASE*** and Eiji SEKINE***

(Received December 23, 1957)

The method now used to produce synthetic mica is to cool a melt having a chemical composition of fluor-phlogopite with small amounts of fluorides and silicates. The cooled mass thus obtained is composed of crystals of fluor-phlogopite with small amounts of glassy substance and fluorides between the mica crystals[1]. The glassy substance binds mica crystals together and makes them difficult to separate from one another.

Further, a thin glass film adhering to the crystals makes them harder and less flexible than natural mica. The quality of mica crystals is often damaged when crystals are separated forcibly.

In order to separate the individual mica crystals more easily and to obtain soft and flexible crystals, agglomerates of synthetic fluor-phlogopite were treated hydrothermally with electrolyte solutions.

Experimental

Samples used were agglomerates of crystals obtained by cooling melts having the following chemical compositions:

I. 3.59 MgO, 0.60 Al_2O_3, 3.00 SiO_2, 0.70 K_2SiF_6
$=K_{1.17}Mg_{3.00}Al_{1.00}Si_{3.09}O_{9.52}F_{3.51}$
$=1.14KMg_3AlSi_3O_{10}F_2+0.13K_2SiF_6+0.16MgSiF_6$
$+0.01MgF_2+0.06AlF_3$

II. 0.50K_2O, 1.88MgO, 1.13MgF_2, 0.50Al_2O_3, 3.00SiO_2
$=KMg_3AlSi_3O_{9.88}F_{2.24}$
$=0.80KMg_3AlSi_3O_{10}F_2+0.15MgF_2$
$+0.05KAlSi_3O_8$ (POM2)[1]

All of these agglomerates contained small amounts of glassy substance and fluorides.

Small pieces of the agglomerate mass, together with an aqueous solution of electrolyte, were placed in an autoclave and heated for one or two days at a temperature within the range 150 to 350°C. The ease of separating individual crystals and the flexibility of separated crystals were tested qualitatively. The fluorine content of the original and treated samples was determined and the weight decrease at various temperatures was measured by a thermobalance. The ease of separation is evaluated by grades A_0, A, B and C. Grade A means that the separation is as easy as that of natural muscovite; grade C is the same as that of untreated agglomerate; grade B is between A and C, and A_0 is better than A.

Results

1) Treatment with sodium hydroxide solution.—(*a*) *Effects of concentration of solution and of period of treatment.*—Results of experiments are given in Table I.

TABLE I

Sample No. 1—fluorine content 13.9 %, Temperature of treatment: 350°C.

Experiment	No. 1	No. 2	No. 3	No. 4	No. 5
Condition for treatment					
Concn. of NaOH solution (N)	0	0.5	1.0	2.0	2.0
Period (hr.)	24	24	24	24	48
Properties of the product					
Ease of separation	C	B	B	A	A
F content (%)	13.5	13.7	13.0	11.2	8.6
Percentage decrease of F	3	1	7	19	38
W. loss between 600° and 850°C (%)	0.0_7	0.1_0	0.1_1	0.1_8	0.3_1

Sample No. 1 contained free fluorides and had a larger fluorine content than that of pure fluor-phlogopite with the theoretical content of 9.04 %. Treatment with tap water for 24 hr. at 350°C had no effect of making separation easier. Treatment with

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1) a) T. Noda and S. Sugiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **46**, 1082 (1943). b) T. Noda, *J. Am. Ceram. Soc.*, **38**, 147 (1955).

TABLE II

Sample No. 1—fluorine content 13.9%, Temperature: 350°C, Period: 48 hr.

Experiment	No. 5	No. 6	No. 7	No. 8
Treating solution	2N NaOH	0.95 mol. NaF / 1·2N NaOH	5.1 mol. $KF \cdot 2H_2O$ / 1·2N NaOH $\left(=\frac{\text{4.3 mol. KF}}{\text{1·1.7N NaOH}}\right)$	0.27 mol. Na_2SiF_6 / 1·2N NaOH
Properties of product				
Ease of separation	A	A	A_0	A
F content (%)	8.6	11.2	10.0	12.7
Percentage decrease of F	38	19	28	9
W. loss between 600° and 850°C(%)	0.3_1	—	0.1_9	0.2_5

0.5 N sodium hydroxide had a weak effect, and that with a more concentrated solution had a stronger effect. Products of experiments Nos. 4 and 5 separated easily and the separated crystals were flexible. The more concentrated the solution and the longer the period of treatment, the greater the decrease of the fluorine content in the product. Temperature-weight loss

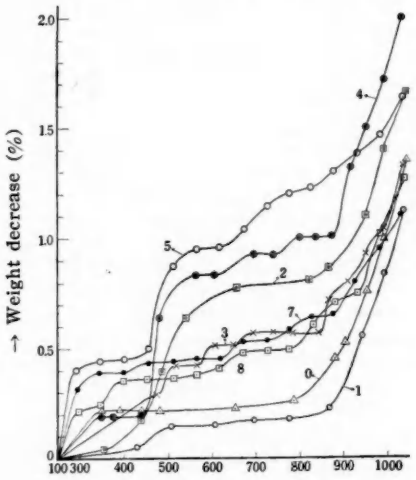


Fig. 1.

curves of these products are given in Fig. 1. The curve for the untreated mass is designated No. 0. In these curves, four stages of weight decrease can be observed, i. e. between 100° and 300°C, between 450° and 550°C, between 600° and 850°C and above 850°C. An agglomerate mass of fluor-phlogopite often occludes gas and carbon. The weight decrease between 100° and 300°C may be due to the evolution of gas and the combustion of carbon. Fluor-phlogopite gradually decomposes and liberates fluorine when heated to above 850°C[2]. These phenomena were verified by the steps of weight decrease observed in the curve of the untreated mass. The glassy substance and fluorides may be changed into hydroxides by these hydrothermal treatments and therefore the weight decrease between 450°C and 550°C is probably due to the decomposition of hydroxides. The weight decrease between 600° and 850°C is related to the dehydration of hydroxyl-phlogopite[3]. It can therefore be concluded that hydrothermal treatments at 350°C with sodium hydroxide solution did produce hydroxides and only the long treatment (No. 5) with concentrated solution changed a part of the fluor-phlogopite into hydroxyl-phlogopite[4].

(*b*) *Effects of addition of fluoride to treating solution.*—As described above, the hydrothermal treatment with sodium hydroxide solution resulted in the change of fluor-phlogopite into hydroxyl-phlogopite. If some equilibrium exists between alkali hydroxide and fluor-phlogopite, such as

$$\text{F-phlogopite} + 2OH^- \rightleftarrows \text{OH-phlogopite} + 2F^-,$$

the hydration of fluor-phlogopite may be suppressed or decreased by the addition of the fluoride ion to the treating solution. Experiments carried out on these lines are given in Table II.

That an addition of fluoride to the solution decreases the percentage decrease of fluorine content of the treated product seems reasonable. The observed decrease in fluorine content of treated products may be due to dissolution of fluoride

2) a) T. Noda and K. Aoki. *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **51**, 7 (1948).
b) T. Noda and T. Matsushita, ibid., **51**, 83 (1948).
3) H. S. Yoder and H. P. Eugster, *Geochim. Cosmochim. Acta*, **6**, 157 (1954).
4) T. Noda and Rustum Roy, *Am. Mineral.*, **41**, 929 (1956).

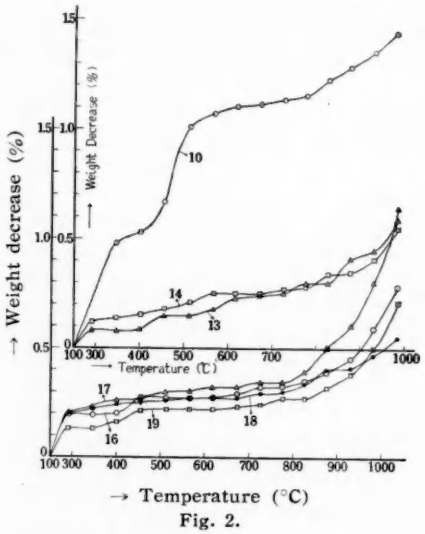
TABLE III

Experiment	No. 9	No. 10	No. 11	No. 12	No. 13	No. 14
Conditions for treatment						
Treating soln.	2N KOH	2N KOH	5.31mol. $KF \cdot 2H_2O$ / 1·2N KOH (= 4.46 mol. KF / 1·1.68N KOH)	3.19mol. $KF \cdot 2H_2O$ / 1·2N KOH (= 2.86 mol. KF / 1·1.80N KOH)	2.13mol. $KF \cdot 2H_2O$ / 1·2N KOH (= 1.98 mol. KF / 1·1.86N KOH)	1.06mol. $KF \cdot 2H_2O$ / 1·2N KOH (= 1.02 mol. KF / 1·1.93N KOH)
Period of treatment (hr.)	12	24	24	24	24	24
Properties of product						
Ease of separation	A	A	A	A	A	A
F content (%)	8.2	7.7	9.2	9.3	9.3	8.7
Percentage decrease of F	41	45	34	33	33	37
W. loss between 600° and 850°C (%)	—	0.1_6	—	—	0.1_4	0.1_0

originally occluded in agglomerate mass. Product No. 7 which was treated with a solution containing 1.7 mol. sodium hydroxide and 4.3 mol. potassium fluoride per liter gave the greatest ease of separation (grade A_0) even though fluor-phlogopite crystals of the product were not changed into hydroxyl-phlogopite.

2) Treatment with potassium hydroxide solution.—(*a*) ***Optimum concentration of potassium fluoride.***—Sample No. 1 having a fluorine content of 13.9 % was used. It seems probable that sodium ion replaces some potassium ion of fluor-phlogopite when sodium hydroxide solution is used as a treating solution. Therefore, the use of potassium hydroxide is prefer able to sodium hydroxide as a treating solution. Treatment with 2 N solution of sodium hydroxide gave the best results for easing separation, but for the reason already given, 2 N solution of potassium hydroxide was used in the following experiments. Experimental results obtained in using 2 N potassium hydroxide with the addition of various amounts of potassium fluoride are given in Table III.

It can be seen in Table III that the effect of potassium hydroxide solution was stronger than that of sodium hydroxide solution. Fluorine contents of the products of experiments Nos. 11, 12 and 13 were nearly equal to the theoretical value of 9.04 %, but those of experiments Nos. 9, 10 and 14 were less than this value. Temperature-weight loss curves of these products are shown in Fig. 2. The product of experiment No. 10 gave 0.40 % of the weight decrease between 450° and 550°C



→ Temperature (°C)

Fig. 2.

which corresponds to the decomposition of hydroxides, whereas the products of experiments Nos. 13 and 14, in which potassium fluoride was added to the treating solution, gave a negligible decrease of weight in the same temperature range. The weight decrease between 600° and 850°C was 0.16 % for the product of experiment No. 10 and that of the products of experiments Nos. 13 and 14 was about 0.1 %. These results indicate that both the formation of hydroxides and the hydration of fluor-phlogopite with hydrothermal treatment were suppressed by the addition of fluoride to the treating solution. The concentration of 1.5 to 2mol.

TABLE IV

Concn. of KF: 2.1 mol. per liter, Temp. of treatment: 350°C, Period of treatment: 24 hr.

Experiment	No. 15	No. 16	No. 17	No. 18	No. 19	No. 20
Concn. of KOH(N)	2	1	0.5	0.25	0.125	0
Properties of product						
Ease of separation	A	A	A	A	B	B
F content (%)	9.4	12.2	12.5	9.3	10.2	10.7
Percentage decrease of F	33	12	10	33	27	23
W. loss between 600° and 850°C(%)	—	0.1_0	0.1_3	0.1_0	0.0_8	—

potassium fluoride per liter was necessary in order to suppress the hydration of fluor-phlogopite in the treatment with 2 N potassium hydroxide.

(*b*) ***Optimum concentration of potassium hydroxide.***—Sample No. 1 having a fluorine content of 13.9 % was used. In the experiments described above the concentration of potassium hydroxide was fixed at 2 N. Table IV shows the results of experiments carried out with potassium hydroxide solution of various concentrations, 2.1 mol. potassium fluoride being added per liter to every treating solution.

A solution containing 2.1 mol. potassium fluoride and no potassium hydroxide had some effect and a concentration of 0.5 N potassium hydroxide with 2.1 mol. potassium fluoride per liter was sufficient to facilitate separation. Curves shown in Fig. 2 indicate no hydration of fluor-phlogopite for these experiments.

(*c*) ***Effect of temperature.***—All experiments hitherto described were carried out at 350°C. When the temperature of treatment is high, the working pressure is consequently high and from a practical standpoint, it is desirable to work with as low temperatures and under as low pressures as possible for the accomplishment of easy separation. Results of experiments using a dilute solution 0.5 N and a concentrated solution (10 N) are given in Table V.

Experiments with 0.5 N potassium hydroxide gave an effect of easing separation when they were carried out at 300°C or above, while in experiments using 10 N potassium hydroxide, treatment at 250°C or above was sufficient to give a good effect. Therefore, the temperature of treatment was fixed at 300°C and the effect of concentration was investigated in experiments given in Table VI.

TABLE V

Period of treatment: 24 hr.
Sample No. 2 having a fluorine content of 9.3% was used.

Temperature of treatment (°C)	350	300	250	200	150
Concn. of KOH					
0.5 N	B	B	C	C	C
10 N	A_0	A	A	C	C

It was found that a solution of 0.25 N potassium hydroxide with 2.1 mol. potassium fluoride per liter was sufficiently strong for easy separation with the treatment at 300°C, as it was with treatment at 350°C.

3) Treatment with acid and salt solutions.—Effects of using acids and some salt solutions as treating solutions for hydrothermal treatment of fluor-phlogopite were investigated because Saito, one of the present authors, had found that hydrothermal treatment of synthetic asbestos with solutions of acids, alkalies or some salts gave easy separation of fiber crystals. Experimental results are given in Table VII.

Treatments with 10 N potassium carbonate solution or with more concentrated solutions gave good results, those with less concentrated solutions had less effect and that with 1 N solution had no effect. Treatments with mixed solutions of 8.4 N potassium carbonate and various concentrations of potassium hydroxide gave the same results as those with mixed solutions of 2.1 N potassium fluoride and various concentrations of potassium hydroxide, as given in Table VI, i. e. treatments with 0.25N potassium hydroxide or more concentrated solutions gave good results. This means that in both cases potassium hydroxide played the main role.

Treatments with hydrochloric acid gave good results when 0.125 N or more concentrated solutions were used. Treatment with potassium hydrogen sulfate gave the best results among those with bisulfate, bicarbonate and biphosphate of potassium.

Fluorides were found to have a suppressing effect on hydration of fluor-phlogopite, and experiments Nos. 27′ to 31′ show that

TABLE VI

Sample No. 1 having a fluorine content of 13.9% was used.
Temp. of treatment: 300°C, Concn. of KF: 2.1 mol. per liter, Period of treatment: 24 hr.

Experiment	No. 21	No. 22	No. 23	No. 24	No. 25	No. 26
Concn. of KOH(N)	2	1	0.5	0.25	0.125	0.0625
Properties of product						
Ease of separation	A	A	A	A	B	B
F content (%)	9.5	13.7	11.0	10.8	10.4	11.7
Percentage decrease of F	32	1	21	23	25	16
W. loss between 600° and 850°C(%)	0.0_7	0.0_5	0.1_7	0.0_6	0.0_8	0.0_7

TABLE VII

Condition I: Temp.: 250°C, Period: 24 hr., except on special notice.
Condition II: Temp.: 350°C, Period: 48 hr.

Experiment	Condition	Treating soln.	Ease of separation
No. 1′	I	11.6N K_2CO_3	A_0
2′	I	10.0N K_2CO_3	A
3′	I	8.4N K_2CO_3	B
4′	I	4.7N K_2CO_3	B
5′	I	1.0N K_2CO_3	C
6′	I	3.0N KOH 8.4N K_2CO_3	A
7′	I	2.0N KOH 8.4N K_2CO_3	A
8′	I	1.0N KOH 8.4N K_2CO_3	A
9′	I	0.5N KOH 8.4N K_2CO_3	A
10′	I	0.25N KOH 8.4N K_2CO_3	A
11′	I	0.125N KOH 8.4N K_2CO_3	C
12′	I	0.0625N KOH 8.4N K_2CO_3	B
13′	I	0.25N HCl	A
14′	I	0.125N HCl	A
15′	I(12 hr.)	0.125N HCl	C
16′	I	0.0625N HCl	B
17′	I	0.0312N HCl	B
18′	I	0.0156N HCl	B
19′	I	0.0078N HCl	C
20′	I	0.125N HCl 4.7N KCl	B
21′	I	0.125N HCl 2.35N KCl	B
22′	I	2.2N $KHSO_4$	A_0
23′	I	1.5N $KHSO_4$	C
24′	I	0.7N $KHSO_4$	C
25′	I	3.0N $KHCO_3$	B
26′	I	2.9N KH_2PO_4	B
27′	I	7.4N KF	A
28′	I(12 hr.)	7.4N KF	B
29′	I	6.2N KF	C
30′	I	5.0N KF	C
31′	II	2.4N KF	A_0
32′	II	H_2O	C

potassium fluoride itself can ease separation of mica crystals.

Crystals treated with acid solutions were found to be harder and less flexible than those treated with alkaline solutions. It seems that the difference in these physical properties of products depends on the different actions of acid and alkali on glassy substance in the agglomerate mass. Alkali reacts on glass to make the silicic acid component of the glass soluble or to accelerate devitrification of the glass, thus decreasing the strength of the glass to bind mica crystals. The dissolution and the devitrification of the glass help the treating solution to penetrate further into the agglomerate mass and react on glass in deep places of the mass. The milk-white substance produced by devitrification of glass which exists between mica crystals in treated agglomerates, was separated easily when the crystals were split from the mass.

Acid reacts on glass to dissolve basic components of glass and leaves the silicic acid component undissolved. The silicic acid skeleton thus produced may prevent penetration of the treating solution into shallow spaces, such as interstices between cleavage planes of mica crystals. This

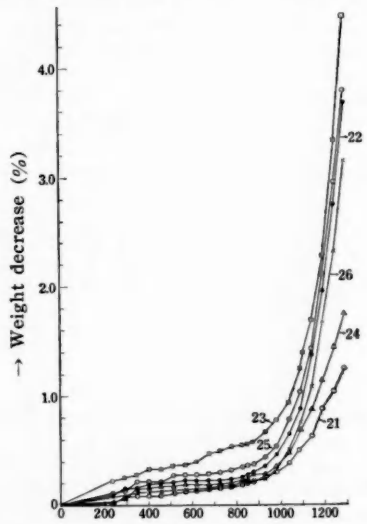


Fig. 3.

makes separation of glassy substance in the acid-treated mass more difficult than separation of glass in the alkali-treated mass and the split crystals from the acid-treated mass are somewhat harder and less flexible than those from the alkali-treated mass.

Hydrothermal treatment for easy separation was much more effective on agglomerates of well developed crystals than on those of small crystals because treating solution penetrates much more easily into the mass along plate crystals than through the mass of irregularly arranged small crystals.

Percentage decreases of fluorine content of the mass treated with potassium carbonate, potassium hydrogen sulfate or hydrochloric acid were found to be smaller than those of the mass treated with alkali by the measurement of fluorine content and temperature-weight loss curve of these products.

4) Investigation on treated mica crystals. — (*a*) *Vacuum test.* — Vacuum characteristics of split mica crystals of untreated synthetic fluor-phlogopite, of products of experiments Nos. 1 to 8 and natural phlogopite were measured. Specimens used for the measurement were washed with ethylalcohol, rinsed with distilled water and dried at 120°C for 1 hr. The specimens were placed in a silica glass tube pumped to a pressure of 1×10^{-5} mmHg. Then the specimens were put into a hot place in the vessel maintained at a definite temperature, and the change of pressure of the vessel was measured. Fig. 4a shows the volume of gas evolved from the specimens when heated. Results of the measurements on specimens which were first outgassed by heating in a high vacuum (1×10^{-5} mmHg) are shown in Fig. 4b. The glassy substance adhering to untreated crystals contains minute amounts of carbon and gas. Hydrothermal treatment decreases the amount of glass adhered. This is why treated crystals evolved smaller amounts of gas than the untreated crystals at temperatures lower than 800°C. Specimen No. 5, which was treated with 2 N sodium hydroxide for 48 hr. and was expected to contain hydroxyl-phlogopite, increased the gas evolution rapidly at about 950°C in the same way as natural phlogopite did. It is worthy of note that specimen No. 7, which was treated with 1.7 N sodium hydroxide in the presence of 4.3 mol. potassium fluoride per liter, evolved the smallest amount of gas among specimens tested.

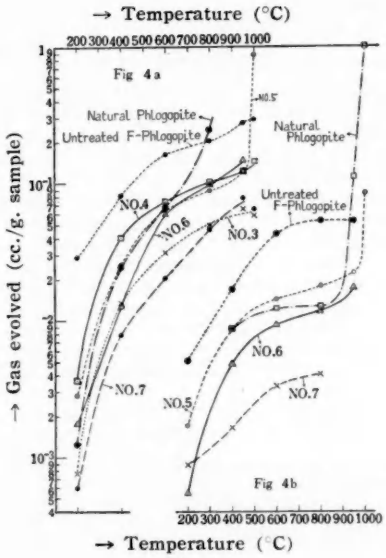


Fig. 4.

(*b*) *X-ray powder diagram.*—It can be said from the experimental results described above that the main part of the original fluor-phlogopite remained unchanged by hydrothermal treatment, although a small part of the mica changed to hydroxyl-phlogopite. X-ray powder photographs taken by using a camera of 114.6 mm. diameter gave no difference between untreated and treated micas. However, by using a Norelco X-ray Geiger counter goniometer, weak extra peaks adjacent to (00*l*) of fluor-phlogopite were detected in the X-ray powder diagram of treated mica which was found to have a weight loss between 600° and 850°C. This means that a small amount of hydroxyl-phlogopite exists in the specimen because these extra peaks correspond to (00*l*) of hydroxyl-phlogopite[4].

Summary and Conclusion

Agglomerates of synthetic mica crystals were treated hydrothermally with alkali, acid and salt solutions in order to ease the separation of mica crystals which are bonded together by glassy substance.

(1) Among treatments with sodium hydroxide solutions of the concentration from 0.5 to 2 N at 350°C for 24 hr., that with 2 N sodium hydroxide facilitated greatly the separation of mica crystals.

A small amount of fluor-phlogopite probably changed to hydroxyl-phlogopite and hydroxides were produced by the hydrothermal treatment.

(2) The hydration of fluor-phlogopite and the formation of hydroxide were suppressed by the addition of fluorides in the treating solution. It was found that the presence of 1.5 mol. potassium fluoride per liter of treating solution was effective for the suppression.

(3) Among treatments with potassium hydroxide solution in the presence of 2 mol. potassium fluoride per liter solution at 350°C for 24 hr., that with 0.25 N or more concentrated solution of potassium hydroxide was effective for easing separation of mica crystals. Potassium fluoride itself was found to be effective for easy separation.

(4) It was necessary to keep the temperature at 250°C or above in the treatment with 10 N potassium hydroxide and 300°C or above in the treatment with 0.5 N potassium hydroxide in order to obtain a good result.

(5) Treatments with potassium hydroxide solution in the presence of 2 mol. potassium fluoride per liter solution at 300°C for 24 hr. were as effective as those with the same solution at 350°C.

(6) Among treatments with solutions of various concentrations of potassium carbonate or potassium carbonate and potassium hydroxide at 250°C for 24 hr., 10 N or more concentrated potassium carbonate solution was effective as a treating solution and in a mixed solution of potassium carbonate and potassium hydroxide the latter played the main role.

(7) Among treatments with solutions of various concentrations of hydrochloric acid or hydrochloric acid and potassium chloride at 250°C for 24 hr., 0.125 N or more concentrated hydrochloric acid solution was effective as a treating solution and the presence of potassium chloride had no effect.

(8) Among treatments with potassium hydrogen sulfate, potassium hydrogen carbonate and potassium dihydrogen phosphate, that with potassium hydrogen sulfate was most effective and the smallest necessary concentration of the treating solution was 2 N.

(9) A solution of 7 N potassium fluoride or a more concentrated one was effective as a treating solution at 250°C for 24 hr.

(10) Split crystals from the mass treated with alkali and potassium fluoride solutions were flexible and those treated with acid were harder and less flexible than the former. The difference of the effects of acid and alkali was interpreted as the difference of their action on binding glass.

(11) Hydrothermal treatment for easy separation was much more effective on agglomerates of well developed crystals than on those of small crystals because the treating solution penetrates easily into the mass along plate crystals.

(12) Investigation of X-ray powder diagram of treated products revealed that the main part of fluor-phlogopite crystals remained unchanged and only a small amount of original mica changed to hydroxyl-phlogopite by treatments with strong alkali solutions. This observation was in good agreement with the experimental results deduced from the observed decreases of fluorine contents and temperature-weight loss curves of treated products.

(13) It was found that split crystals from a treated mass evolved less gas than those from an untreated mass because of the low content of adhering glass in the former. Split crystals which contained a small amount of hydroxyl-phlogopite began to evolve gas at about 950°C.

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Studies on Explosive Reaction of Ethylene Mixed with Oxygen or Air. I. Explosion Limit at Low Pressure

By Masao SUGA

(Received January 13, 1958)

The explosion and the combustion phenomenon of lower hydrocarbons have been studied extensively[1-3], but there are few investigations about ethylene. The explosion of gas has generally very complex mechanism, and various methods have been taken for the determination of the explosion limit[1,4]. The present author, considering conveniently that the spontaneous ignition was the explosion, investigated systematically on the phenomena of spontaneous ignition of ethylene-oxygen or -air mixture at lower pressures than atomospheric. The explosion limit was determinated by so-called "admission method", in which the gas mixture with a certain definite composition was admitted into the reaction vessel evacuated and heated at a definite temperature. The limit was not only decided by some parameters such as temperature, pressure or composition, but was affected considerably by the nature of the surface of the reaction vessel etc. Thus a standard procedure was adopted for convenience in order to determine the limit, and the effects were briefly discussed.

Experimental

Materials.—The ethylene employed in this experiment was prepared by the dehydration of absolute alcohol by the action of phosphoric acid and purified by the action of concentrated aqueous solution of sodium hydroxide, concentrated sulfuric acid, silica gel and phosphorus pentoxide. About 99% of the gas so treated was absorbed by fuming sulfuric acid. The oxygen employed was obtained from a commercial cylinder (purity: 99.4%). The oxygen and the air were used after being passed through a train consisting of two bottles containing a concentrated aqueous solution of sodium hydroxide, concentrated sulfuric acid and phosphorus pentoxide.

1) B. Lewis and N. von Elbe, "Combustion, Flames and Explosions of Gases", Academic Press Inc., New York, (1951).
2) M. Prettre, "Third Symposium on Combustion, Flame and Explosion Phenomena", The Williams and Wilkins Co., Baltimore, (1949), p. 397.
3) K. Spence and D.T.A. Townend, ibid., p. 404.
4) F. S. Dainton, "Chain Reaction", Methuen Co., London, (1956) p. 23.

Apparatus and Procedure.—The diagram of the apparatus is shown in Fig. 1. The apparatus was partly screened with wire netting for the prevention of explosion. The inlet tube connecting the reaction vessel to the cock C_1 and the manometer M_1 was used as capillary to decrease dead space, also to prevent danger. The explosion limit was determined by the following procedures:

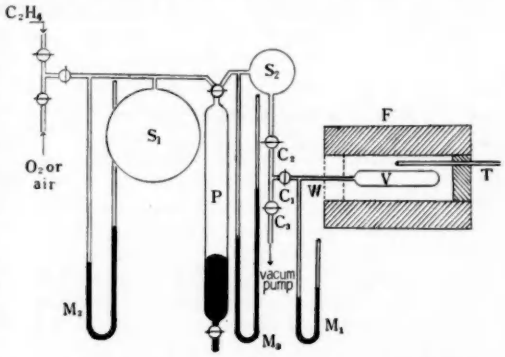

Fig. 1. The apparatus of admission method for determining the explosion limit.
S_1, S_2: Gas storages.
C_1, C_2, C_3: Stop cocks.
M_1, M_2, M_3: Mercury manometers.
P: Toepler pump.
V: Reaction vessel.
F: Electric farnace.
T: Thermocouple.
W: Window.

(1) The gas mixture of the desired composition for the test was prepared in storage S_1 (1 l.), the partial pressures of gases being measured by the manometer M_2, and stored for more than twelve hours in order to be thoroughly mixed.

(2) Then, a part of sample gas in storage S_1 was removed into storage S_2 (ca. 200 cc.) at any desired pressure by the aid of Toepler pump P.

(3) The reaction vessel V (usually 3 cm. diameter and 10 cm. length in order to examine the effect of diameter on the limit, 2 cm. or 1 cm. diameter and equal length) which consisted of a quartz cylinder was placed in a horizontal electric furnace F. The highest temperature in furnace F was measured by an alumel-chromel thermocouple T inserted into furnace F. On this occasion, the reaction vessel was maintained at a definite temperature and

thoroughly evacuated (10^{-3} mmHg) in thirty minutes.

(4) The sample gas in storage S_2 was rapidly admitted to pre-evacuated reaction vessel V to give some previously decided initial pressure by operating cocks C_1 and C_2.

(5) The determination of the occurence of explosion or otherwise was made directly by sight through the window W made of mica on one side of the furnace and subsidiarily by the pressure change with the aid of mercury manometer M_1 for thirty minutes.

The induction period, which is the time-lag from the moment of admission of the sample gas to the occurrence of the explosion, was measured by the aid of a stopwatch. Isochors (pressure-temperature diagram) of the explosion limit were determined by the repetition of these procedures 2—5, at the temperature range between 300 and 700°C, and at the pressure range lower than atomospheric pressure for various compositions. Then, these were used to derive isotherms and isobars.

Results and Consideration

Observation.—The results of observation are classified as the following.

(1) After the lapse of various induction periods (usually less than 30 sec.) luminous flames were normally preceded by a glow which rapidly built up into a bright flash filling the vessel and accompanied by a vigorous pulse and sound.

(2) After the lapse of the relatively long induction periods, pale blue flames were observed in the dark room with a mild pressure pulse which was measured with much difficulty by mercury manometer M_1.

(3) After a considerable time interval (the so-called induction period of slow reaction), the pressure gradually rose, and the maximum pressure was maintained for an appreciable period before slowly falling off. But ignition flames were not able to be found even in the dark room.

(4) No change was observed.

Case 1 and 2 are considered to be the explosions.

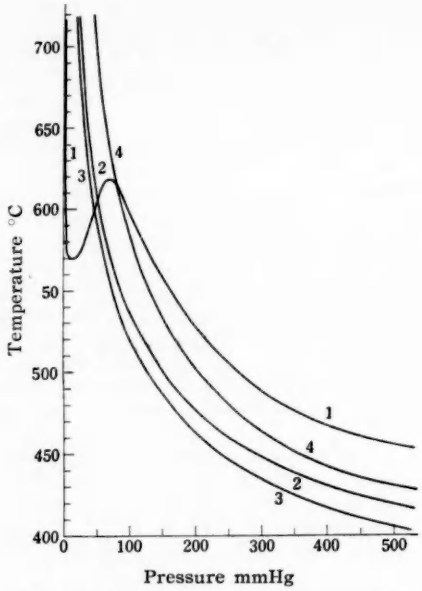

Fig. 2. Isochors for explosion limit of ethylene-oxygen mixtures. curve 1= 20%, 2=40%, 3=60%, 4=80% ethylene.

The Explosion Limit of Ethylene-Oxygen Mixtures.—Isochors were determined for the mixture of the various compositions. Only a certain number of isochors are shown in Fig. 2. Only the

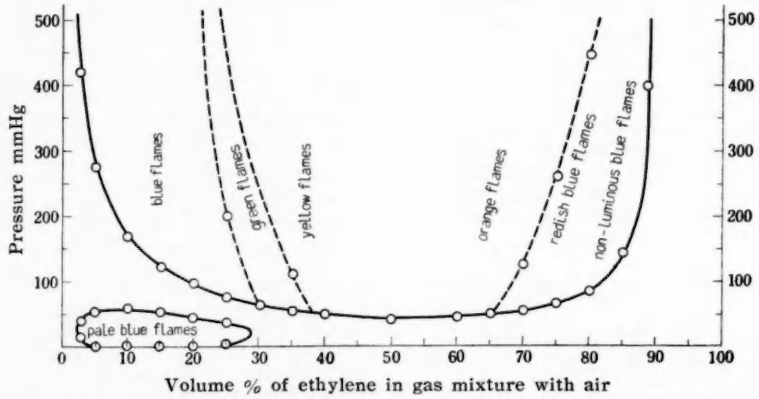

Fig. 3. Isotherm for explosion limit of ethylene-oxygen mixtures at 600°C.

600°C isotherm is shown Fig. 3. The curves shown in these figures exhibit the minima at the composition of about 50% ethylene and are situated about 2.5~90% ethylene. The explosion limit peninsula as indicated in Fig. 2 (curve 1) is found on the definite temperature and pressure condition in the mixture range 2.5~30% ethylene as indicated in the lower closed curve in Fig. 3.

a) Non-luminous blue flames are the flames observed in the ignition of the mixture of more than 70% ethylene. The pressure pulses are relatively mild in company with the flames, and no propagating flames are observed.

b) Luminous blue flames are the flames observed in the ignition of the mixture of less than 30% ethylene. Even at a lower pressure region, the pressure pulses are relatively violent with the flames and propagating flames are often observed.

c) Luminous yellow flames are the flames observed in the ignition of the mixture of 20~80% ethylene. The flames are propagated into the inlet tube of the reaction vessel, with vigorous pulses.

d) Luminous green flames are the flames observed in the ignition of the mixture of about 35% ethylene.

As a whole, the color of ignition flames, as shown in Fig. 3, changes in the order of blue, yellow, green and blue, with decrease of the percentage of ethylene.

Morever, as a remarkable phenomenon, in the mixture range 60~80% ethylene, reddish blue flames are often observed and a small quantity of deposited carbon is found on the wall of the reaction vessel V and capillary inlet tube connecting the reaction vessel V to cock C_1 and manometer M_1. The flames in the explosion peninsula are very faintly visible after the longer induction periods (10 sec.~20 min.) as described in 2). The boundary between the second and the third (thermal)

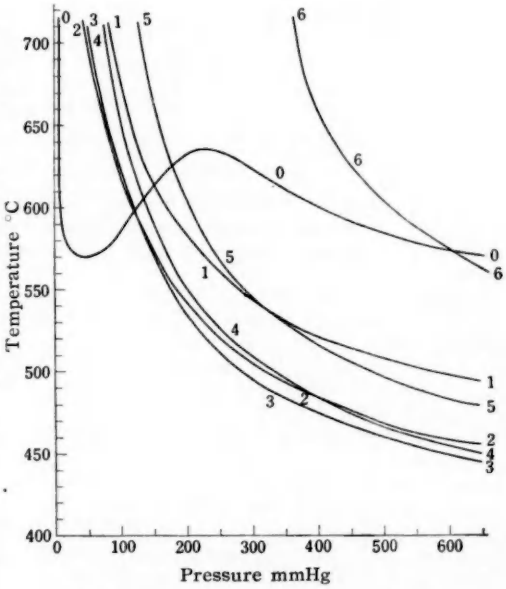

Fig. 4. Isochors for explosion limit of ethylene-air mixtures. curve 0=5%, 1=10%, 2=20%, 3=30%, 4=40%, 5=50%, 6=60% ethylene.

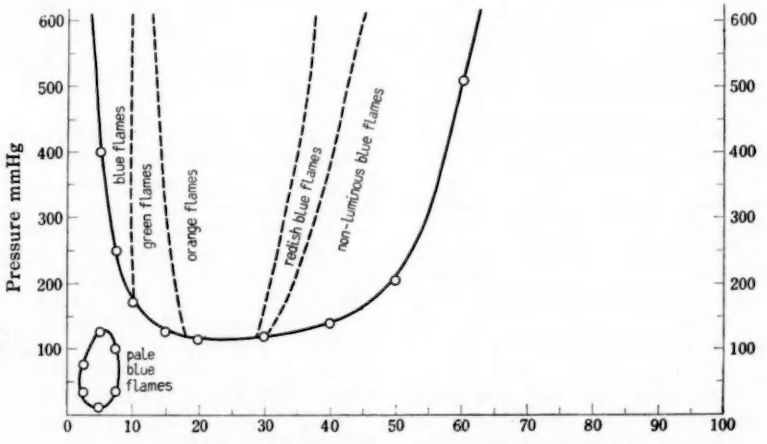

Fig. 5. Isotherm for explosion limit of ethylene-air mixtures at 600°C.

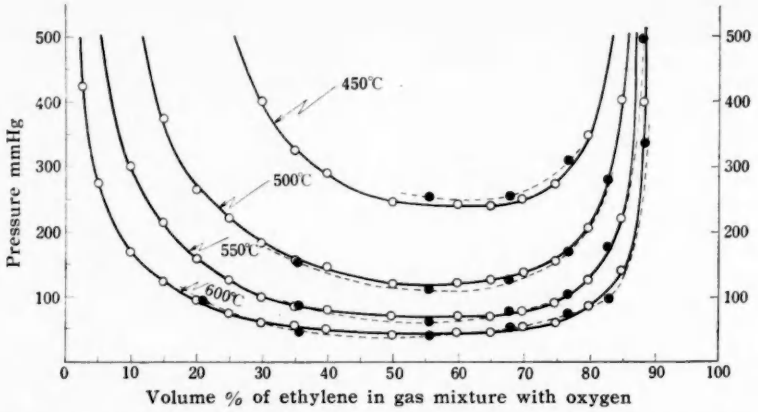

Fig. 6. Relationship between isotherms for explosion limit of ethylene-oxygen and ethylene-air. (Broken lines represent the data calculated from the limit of ethylene-air mixtures, illustrated in considerations.)

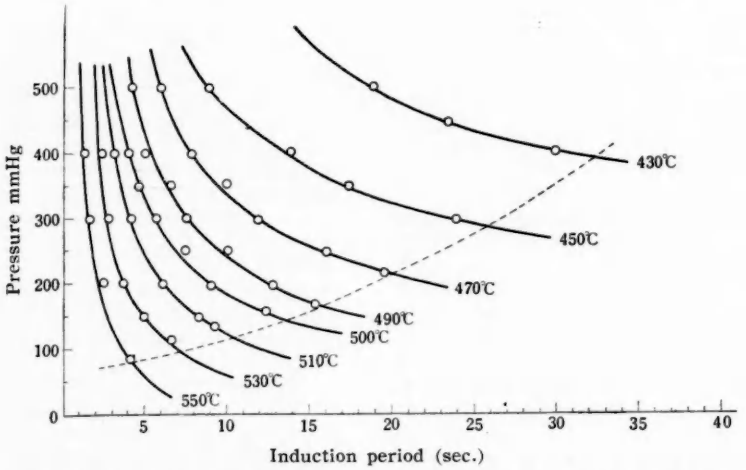

Fig. 7. Relationship between explosion limit pressure and induction period at a definite temperature.

limit was accurately determined with difficulty in the present experimental method.

The Explosion Limit of Ethylene-Air Mixtures.—Isochors of the explosion limit at the compositions of 5, 10, 20, 30, 40, 50 and 60% ethylene with air can be obtained by the same method described as with oxygen and shown in Fig. 4. Also the 600°C isotherm is shown Fig. 5.

In order to elucidate the effect of the foreign gas, N_2, the limiting pressures and composition of ethylen-air mixtures at temperatures of 600, 550, 500 and 450°C are converted in to those of ethylene-oxygen mixtures by calculation, subtracting the partial pressure of nitrogen. These calculations give the broken lines in Fig. 6 which shift little from the corresponding full lines except the second pressure limit. A further investigation of the second pressure limit is now in progress. In addition, the ignition flames are the same as ethylene with oxygen, and may lead to the conclusion that the effect of nitrogen on the first and the third pressure limit should be negligible.

The Explosion Limit and Induction Period.—The results of the experiment with regard to the induction period are shown in Fig. 7. Generally, the higher the admission pressure, the shorter the

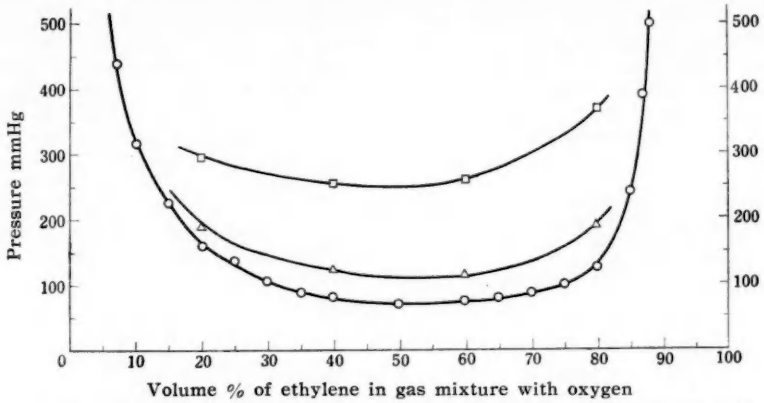

Fig. 8. (a) Effect of reaction vessels diameter for the isotherms at 550°C.
Diameter: □, 1 cm; △, 2 cm; ○, 3 cm.

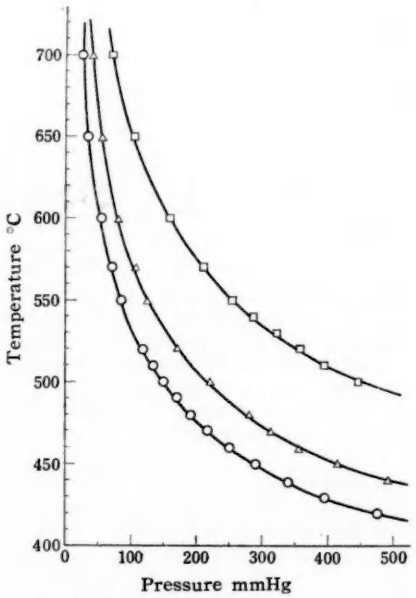

Fig. 8. (b) Effect of reaction vessel diameter for the isochors of 40% ethylene.
Diameter: □, 1 cm; △, 20 cm; ○, 3 cm.

induction period. The influence of temperature is greater than that of pressure.

In consequence, the induction periods, over 650°C, became less than one second and accordingly can not be measured with a stopwatch with accuracy. Slow reactions also had the induction periods which were longer than those of explosions, but the quantitative relationship could not be described in the present experiment. Also as a remarkable phenomenon, preceding the ignition, the pressure changes which anticipated the explosion were often observed by mercury manometer M_1.

The Effect of Reaction Vessel.—The reaction vessels used were usually quartz cylinders of 3 cm. in diameter and 10 cm. in length. Quartz cylinders of 2 cm. or 1 cm. in diameter of the same length were also employed in order to examine the effect of the diameter of reaction vessels. The result is indicated in Fig. 8. The decrease of the vessel diameter serves invariably to retard the explosion. The quantitative relationship can not be discussed in detail. Furthermore it was found that the result varied with previous history of the reaction vessel (e.g. the quality and time of pumping during evacuation of the vessel between experimental runs), and that the induction period was greatly influenced. But these effects were not reproducible, so the present authors adopted the standard procedure as follows.

After the previous runs, the reaction vessel was heated to 600°C and evacuated to 10^{-3} mm Hg (tested by Gaisler tube) for thirty minutes. The virgin vessels were employed after explosive runs. It is confirmed that the experiments with these precaution are reproducible and the results are probably always reliable.

The Activation Energy of the Reaction. — In Fig. 9 is shown the relationship between $\log_{10} p/T$ and $1/T$ for the third limit of Fig. 2. Those graphs are essentially linear at a lower temperature than 600°C and adhere to the relationship $\log_{10} p/T = A/T + B$. If the ignition limit is thermal in character, the gradient of

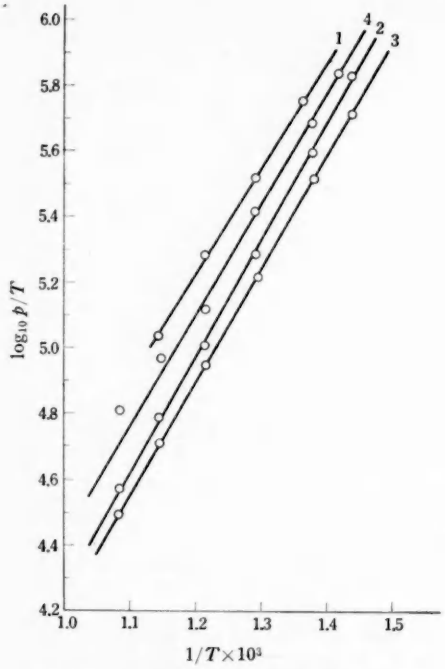

Fig. 9. $\text{Log}_{10}\, p/T$ against $1/T$ curves for the explosion limit of ethylene-oxygen mixtures. curve 1=20%, 2=40%, 3=60%, 4=80% ethylene.

these lines A will be equal to $E/2.303\times 2\times R$.[5,6] Thus values for E, the apparent activation energy, may be calculated as in Table I.

TABLE I
ACTIVATION ENERGIES ESTIMATED FROM SPONTANEOUS IGNITION LIMITS OF ETHYLENE-OXYGEN MIXTURES

C_2H_4%	A	$E=2.303\times2\times1.987\times A$ (kcal./mol.)
80	3.18	29.10
60	3.74	34.23
40	3.47	31.76
20	3.37	30.84

On the other hand, in Fig. 10 is shown the relationship between $\log_{10}\tau = A'/T + B'$. There will be only an in direct meaning of the kinetics, but the gradient of these lines A' is thought to be equal to $E/2.303\times R$.[7] Thus values for E', the apparent activation energy, may be as in Table II.

5) K. Semenoff, *Z. Physik.*, **48**, 57 (1928).
6) K. Posthmus, *Rev. Trav. Chim.*, **49**, 309 (1930).
7) B. P. Mullins; "Spontaneous Ignition of Liquid Fuels", Butter Worths Sci. Pub., London, (1955).

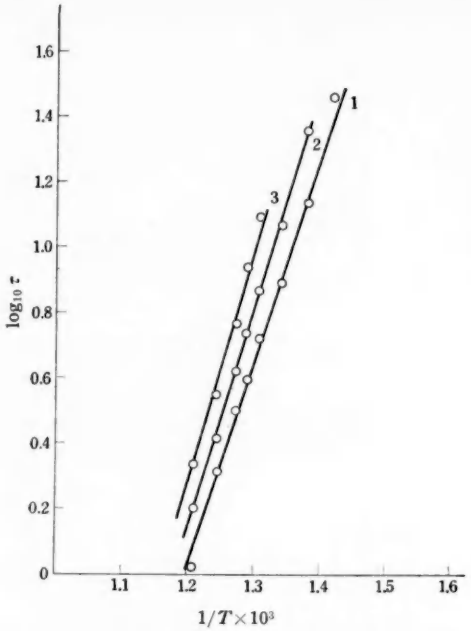

Fig. 10. $\text{Log}_{10}\,\tau$ against $1/T$ curves for the explosion of 40% ethylene-oxygen mixture. curve 1=400, 2=300, 3=200 mmHg.

TABLE II
ACTIVATION ENERGIES ESTIMATED FROM THE INDUCTION PERIODS

Admission pressure (mmHg)	A'	$E=2.303\times1.987\times A'$ (kcal./mol.)
400	6.05	27.69
300	6.52	29.84
200	7.12	32.58

The explosive reactions of ethylene with oxygen or air may be considered to be thermal in apparent character in the present experimental ranges.

Summary

The explosion limit of ethylene mixed with oxygen or air was determined at lower pressure than atomospheric pressure by the statical constant volume method known as the "admission method". Isochors, isotherms and isobars of the explosion limit have been shown. The colors of ignition flames change in the order of blue, yellow and blue with the decrease in the percentage of ethylene. In addition, the explosion peninsula was recognized at a definite condition in the mixture range 2.5~30% ethylene in

oxygen. The results of ethylene with oxygen and ethylene with air were equivalent to each other, so far as the partial pressure of nitrogen was neglected. Induction periods were also taken into consideration and the apparent activation energy was estimated to be about 30 kcal./mol.

The author wishes to thank the late Professor R. Kiyama and Dr. Z. Ôsugi of the Kyôto University and Professor T. Kôzu for their kind advice and encouragement throughout this work. He is also grateful to Mr. K. Ochi, Mr. T. Ogura and Mr. M. Siga for the assistance of observations done partly in the present experiment.

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Colorimetric Determination of Bivalent Copper Using Sodium Alizarin-3-Sulfonate as a Reagent

By Anil K. MUKHERJI* and Arun K. DEY

(Received October 1, 1957)

Sodium alizarin-3-sulfonate, commonly known as the dye Alizarin Red S (abbreviated as ARS), has been widely used in the determination of aluminum[1], and has also found application in the analysis of zirconium and hafnium[2]. Raghava Rao and coworkers[3] have suggested the use of the reagent in the colorimetric determination of uranium and thorium and Rinehart[4] for the estimation of rare earths. In a recent communication Mukherji and Dey[5] reported the formation of colored lakes of various metals with Alizarin Red S and suggested that the reagent might be of use in other determinations as well.

In further communications Mukherji and Dey have reported the spectrophotometric study of alizarin sulfonate chelates of cupric[6] and lead[7] and have also discussed the structure of alizarin sulfonate chelates of bivalent metals[8]. It has been found that copper forms a 1:1 chelate with sodium alizarin-3-sulfonate with λ_{max} at 500 mμ. In this paper we are reporting our observations on the possibility of using the reagent for the colorimetric determination of bivalent copper on a micro-scale.

Experimental

Solutions of cupric sulfate (BDH Analar) and of Alizarin Red S (BDH Indicator) were prepared in carbon-dioxide free water and standardised as usual. The spectrophotometric measurements were carried out in an air conditioned room maintaining a constant temperature of 25°C.

Absorption spectra of the chelate.—The absorption spectra of the reagent using 0.0002 M solution and the chelate (1 : 1 mixture of the reagent and cupric sulfate of the same concentration) were studied at different wave lengths. The optical densities were measured with an SP 500 spectrophotometer, manufactured by Unicam Instruments Ltd. The thickness of the solution was 1 cm. in glass cells supplied with the instrument. pH of both solutions was 4.3. The results are plotted in Fig. 1.

Conformity to Beer's law.—To fixed volumes of ARS solution were added varying volumes of

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1) J. H. Yoe, "Photometric Chemical Analysis", Wiley, New York (1928); F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis", Van Norstand, New York, (1928); "B. D. H. Book of Organic Reagents", Poole (1949).

2) D. E. Green, *Anal. Chem.*, **20**, 370 (1948); J. C. Griess, Jr., U. S. Atomic Energy Comm. Rept., KAPL, 305 (1950); A. Mayer and G. Bradshaw, *Analyst*, **77**, 476 (1952); G. B. Wengert, *Anal. Chem.*, **24**, 1449 (1952); D. L. Manning and D. C. White, ibid., **27**, 1389 (1955).

3) K. S. Venkataswarlu and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, **13**, 79 (1955); D. V. N. Sarma and Bh. S. V. Raghava Rao, ibid., **13**, 142. (1955).

4) R. W. Rinehart, *Anal. Chem.*, **26**, 1820 (1954).

5) A. K. Mukherji and A. K. Dey, *Proc. Natl. Acad. Sci., India*, **27A**, 2421 (1957).

6) Idem., *J. Ind. Chem. Soc.*, **34**, 461 (1957).

7) Idem., *Proc. Natl. Acad. Sci., India*, **27A**, 20 (1957).

8) Idem., *Vi jñāna Pari. Anu. Patrikā*, **1**, 23 (1958).

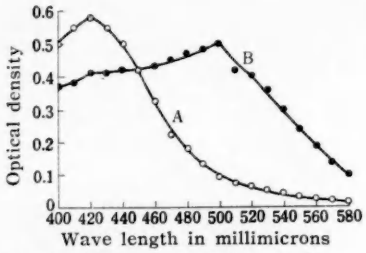

Fig. 1. Absorption spectra studies.
Curve A: Sodium alizarin-3-sulfonate 0.0002 M; Curve B: 1 : 1 mixture of sodium alizarin-3-sulfonate and cupric sulfate (0.0002 M).

cupric sulfate solution, keeping in view that the amount of the chromophoric agent remained in large excess as compared to cupric sulfate. The total volume was kept constant by the addition of water. The optical densities of 1 cm. thickness of the solutions were measured with the spectrophotometer. The observations were repeated at three wave lengths as noted in Table I:

TABLE I

Concn. of Cupric Sulfate $=1.0\times10^{-4}$ M
Concn. of ARS $=1.0\times10^{-3}$ M
Volume of ARS taken =10 ml.
Total Volume =50 ml.

Volume of $CuSO_4$ ml.	Optical density		
	450 mμ	500 mμ	550 mμ
0	0.410	0.080	0.025
2	0.420	0.140	0.065
4	0.425	0.186	0.095
6	0.430	0.215	0.105
8	0.430	0.245	0.125
10	0.435	0.280	0.145
12	0.440	0.300	0.155
14	0.440	0.340	0.170
16	0.445	0.350	0.185
18	0.445	0.360	0.195
20	0.450	0.380	0.200

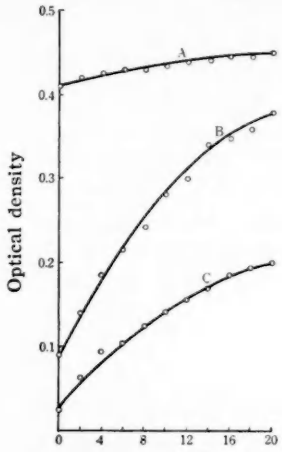

Fig. 2. Conformity to Beer's law.
Curve A, 450 mμ; Curve B, 500 mμ; Curve C, 550 mμ.

The results in Table I are represented graphically in Fig. 2. It may be seen that the calibration curves have a curvature, which is probably due to the colloidal nature of the reagent[9].

Stability of the color at room temperature.—A mixture of solutions of 0.0002 M of cupric sulfate and 0.001 M of ARS (pH of mixture 4.0) gave the same optical density even after 72 hours of standing at room temperature, showing that the color is stable enough for colorimetric measurements.

Influence of temperature.—The color intensity remains constant over a temperature range 20° to 35°C, as may been in Table II:

Influence of pH.—The intensity of color is stable between pH 3.20 to 7.50, as may be seen in Table III:

Sensitivity of the reagent.—The smallest amount of cupric ion that can be detected with Alizarin Red S is 6.4 p. p. m., when absorbance measurements are done in 1 cm. cells.

TABLE II

Concn. of cupric sulfate =0.0002 M
Concn. of ARS =0.001 M
pH of mixture =4.00

Temperature °C	20	25	30	35	40	45
Optical density per cm. (500 mμ)	0.680	0.680	0.680	0.680	0.685	0.685

TABLE III

Concn. of cupric sulfate =0.00005 M
Concn. of ARS =0.0002 M
Temperature =25°C

pH	2.80	3.20	4.00	5.30	6.20	7.50	8.10
Optical density per cm. (500 mμ)	0.420	0.740	0.740	0.740	0.740	0.740	0.440

9) Idem., *Kolloid-Z.*, in press.

TABLE IV

Concn. of cupric sulfate = 0.0002 M (12.7 p. p. m.)
Concn. of ARS = 0.001 M
pH of the mixture = 4.00±0.50
Temperature = 25°C

Ion	Added as	Concn. of ion p. p. m.	Observed change in optical density %	Tolerance limit p. p. m.
Ag^+	$AgNO_3$	9	+ 5	0
Tl^+	Tl_2SO_4	96	+ 3	32
		32	+ 1	
Pb^{2+}	$Pb(NO_3)_2$	16	+20	0
Hg_2^{2+}	$Hg_2(NO_3)_2$	32	−11	2
		2	− 1	
Hg^{2+}	$HgCl_2$	16	− 3	6
		6	− 1.5	
Bi^{3+}	Bi-oxalate	80	Turbid	0
Cd^{2+}	$CdCl_2$	45	+ 3	30
		30	+ 2	
AsO_3^{3-}	H_3AsO_3	82	− 4	41
		41	− 2	
Sb^{3+}	$Sb_2(SO_4)_3$	76	Turbid	0
Fe^{3+}	$FeCl_3$	Interferes at all concn.		0
Fe^{2+}	Ferrous ammonium sulfate	Interferes at all concn.		0
Al^{3+}	$Al(NO_3)_3$	Interferes at all concn.		0
Cr^{3+}	$CrCl_3$	16	+ 3	8
		8	+ 1.5	
Mn^{2+}	$MnSO_4$	80	+ 4	40
		40	+ 2	
Zn^{2+}	$ZnSO_4$	11	+ 3	6
		6	+ 2	
Ni^{2+}	$NiSO_4$	80	+ 4	40
		40	+ 2	
Co^{2+}	$CoSO_4$	50	+ 3	30
		30	+ 2	
Ba^{2+}	$BaCl_2$	55	+20	0
Sr^{2+}	$SrCl_2$	21	+ 3	10
		10	+ 2	
Ca^{2+}	$Ca(NO_3)_2$	32	+ 3	18
		18	+ 2	
Mg^{2+}	$MgSO_4$	10	+ 3	6
		6	+ 2	
Be^{2+}	$BeSO_4$	20	+ 4	8
		8	+ 2	
Zr^{4+}	$ZrO(NO_3)_2$	Interferes at all concn.		0
UO_2^{2+}	UO_2SO_4	Interferes at all concn.		0
Th^{4+}	$ThCl_4$	19	+ 3	10
		10	+ 2	
Ce^{3+}	Cerous ammonium sulfate	22	− 3	11
		11	− 1.5	
Ce^{4+}	$Ce(SO_4)_2$	12	− 4	2
		2	− 1	
WO_4^{2-}	Na_2WO_4	20	−11	0
MoO_4^{2-}	$(NH_4)_2MoO_4$	Interferes at all concn.		0
VO_3^-	NH_4VO_3	Interferes at all concn.		0
SeO_4^{2-}	K_2SeO_4	12	− 3	6
		6	− 2	
TeO_3^{2-}	K_2TeO_3	Interferes at all concn.		0
CO_3^{2-}	Na_2CO_3	20	+ 3	5
		5	+ 1	
SO_4^{2-}	K_2SO_4	152	− 0.5	Large excess
Cl^-	KCl	100	− 1	Large excess
Br^-	KBr	128	− 3	64
		64	− 2	
I^-	KI	50	− 3	30
		30	− 2	
ClO_3^-	$KClO_3$	34	− 3	20
		20	− 2	
BrO_3^-	$KBrO_3$	51	− 3	16
		16	− 1	
IO_3^-	KIO_3	70	+ 3	20
		20	+ 1	
F^-	NaF	8	− 6	0
SiO_3^{2-}	Na_2SiO_3	31	− 3	20
		20	− 2	
Citrate	Sodium citrate	76	− 3	40
		40	− 2	
Tartrate	Potassium tartrate	60	− 5	20
		20	− 2	
Oxalate	Ammonium oxalate	34	− 4	9
		9	− 1	
NO_3^-	KNO_3	80	− 2.5	60
		60	− 1.5	
CNS^-	KCNS	48	− 3	24
		24	− 1.5	
PO_4^{-3}	Na_2HPO_4	38	+ 8	8
		8	+ 2	
$S_2O_8^{-2}$	$K_2S_2O_8$	80	− 3	60
		60	− 2	
HCO_3^-	$NaHCO_3$	10	− 2.5	4
		4	− 1	
$S_2O_3^{2-}$	$Na_2S_2O_3$	45	− 3	25
		25	− 2	
Acetate	Sodium acetate	Interferes at all concn.		0
$B_4O_7^{2-}$	$Na_2B_4O_7$	13	+ 8	0

Influence of foreign ions.—The effect of a large number of cations and anions on the color intensity was studied with the help of the spectrophotometer. The tolerance limits were quantitatively determined. The tolerance limit represents the concentration of a foreign ion, which would affect the optical density of the solution under investigation by less than ±2%. The results are given in Table IV.

Recommended Procedure

For the determination of copper, a solution is prepared and treated to separate the interfering substances as usual[1,10]. The pure copper salt solution thus obtained, is treated directly or with an aliquot portion with a ten-fold molar excess of a freshly prepared aqueous solution, of the reagent. The pH of the solution is adjusted between 4 and 6. The optical density of the solution is then read at 500 mμ, in an absorption cell of suitable thickness. The color intensity can also be measured with a photoelectric colorimeter with an appropriate filter. The temperature of observation should preferably be 20~30°C.

10) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience Publishers, Inc., New York (1950), 295.

Summary

The formation of a 1:1 copper chelate with sodium alizarin-3-sulfonate, having λ_{max} at 500 mμ has been reported. The color formation has been applied to the colorimetric determination of copper on a micro-scale. The color has been found to be stable between pH 3.20 and 7.50, at temperatures 20~30°C. The sensitivity of the reagent is 6.4 p.p.m. of the copper ion. The interference by a large number of cations and anions has been studied and the tolerance limits are quantitatively determined spectrophotometrically. It has been recommended that the reagent is suitable for the colorimetric determination of copper(II) on a micro-scale and the conditions have been prescribed.

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Further Notes on the Ideal Mixture Law for Viscosity

By Tetsuya ISHIKAWA

(Received January, 23, 1958)

Six years ago the author published a paper[1] on the same subject as the above. The previous paper treated the comparison of the validity among the viscosity formulae of Kendall, Macleod, Drucker and Kassel, and Ishikawa with four examples of binary mixtures of the same crystal forms, three being the systems of AgBr-AgCl, $CdCl_2$-$CdBr_2$, and $PbBr_2$-$PbCl_2$, and one being Na-K system, but the present author has thrown some doubt since then on the result of the last pair whose K (Ishikawa's characteristic constant) takes a unique but abnormally greater value, 2.54, throughout the wide temperature range from 103.7 to 192.8°C than the values not so much different from unity for ordinary mixtures composed of like liquids. This paper is intended as a supplementary report on this subject.

Relation between the Formulae—In order to carry on further study, we must consider the relationship between these formulae. For convenience, sake we adopt the following symbols: η_1, η_2 and η signify the viscosities of component 1, 2, and the mixture respectively, φ_1, φ_2 and φ the fluidities of components 1, 2, and the mixture respectively; x_1, x_2, and x so called Macleod's free spaces of 1 cc. of components 1, 2 and the mixture respectively; a_1, a_2 and a the association degrees of component 1, 2 and the mixture respectively and z, z_m and z_v the weight, molar, and volume fraction of component 2 respectively before mixing.

1) T. Ishikawa, This Bulletin, **25**, 38 (1952).

Macleod's formula for ideal mixtures[2]:

$$\left.\begin{aligned}\eta &= \eta_1(1-z_m)\frac{x_1}{x}+\eta_2 z_m\frac{x_2}{x}\\ x &= x_1(1-z_v)+x_2 z_v\end{aligned}\right\} \quad (1)$$

Drucker and Kassel's formula[3]:

$$\varphi=\varphi_1(1-z)+\varphi_2 z \quad (2)$$

This formula can also be obtained from Macleod's relation, $\eta=K_M Ma/x$ (M is the molecular weight and K_M so called "a universal constant" according to his theory[4], and another assumable relation which becomes identical with Macleod's relation for x in Formula 1 in the case of gaseous state where $z_v=z_m$, and $a_1=a_2=a=1$:

$$\frac{x}{a}=\frac{x_1}{a_1}(1-z_m)+\frac{x_2}{a_2}z_m \quad (3)$$

Ishikawa's formula for ideal mixtures[5]:

$$\eta=\eta_1\frac{k_1a_1(1-z_m)}{k_1a_1(1-z_m)+k_2a_2z_m}+\eta_2\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z_m} \quad (4)$$

where k_1 and k_2 denote so-called "field constants" of component 1 and 2 respectively according to his theory.

Now if we transform Formula 2 and 4 into hyperbolic forms, we obtain for Drucker and Kassel's formula, remembering $(1-z)/z=(1-z_m)M_1/z_mM_2$,

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{\varphi_2M_2}{\varphi_1M_1} \quad (5)$$

and for Ishikawa's formula,

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{k_2a_2}{k_1a_1}=K \quad (6)$$

Among 63 kinds of liquid pair which satisfy Formula 6[6], there occur four cases, for which Formula 5 holds good with nearly equal values of $\varphi_2M_2/\varphi_1M_1$ and K: trichloroethylene–pentachloroethane, ethyl propionate–propylacetate, toluene–bromobenzene and *m*-cresol–*p*-cresol (see Table I in which parentheses denote the association degrees quoted from Bingham and Spooner's table[7]).

Since each of these pairs consists of the liquids having nearly equal association degrees, i.e., $a_1=a_2$, there may undoubtedly exist the following relation, comparing Formula 6 with Formula 5:

$$\frac{k_2}{k_1}=\frac{\varphi_2M_2}{\varphi_1M_1},\ \text{or}\ K=\frac{\varphi_2M_2a_2}{\varphi_1M_1a_1} \quad (7)$$

From relation 7, it may easily be understood that the fundamental additive law for viscosity with respect to molar fraction:

$$\eta=\eta_1(1-z_m)+\eta_2z_m \quad (8)$$

is valid only for such pairs where Gartenmeister's relation, $\eta=k_GM$, k_G being a constant[8], holds good and at the same time the condition, $a_1=a_2$, is satisfied

A New Method for evaluating Association Degrees—As regards the evaluation of the association degrees of liquids, a few methods have been proposed by several investigators[9-12]. They are individually no other than deviation factors from a statistically deduced constant in some physico-chemical relation which fits normal liquids, so that for the values of highly associated liquids, there is no means among themselves for confirming whether they are probable values or not.

On the other hand, if relation 7 is applied to evaluate the association degrees of liquids, it is convenient to ascertain their values, since for three ideal mixtures, A—B, B—C, and C—A, there exists the known relation:

$$\frac{k_Aa_A}{k_Ba_B}=\frac{k_Aa_A}{k_Ca_C}\cdot\frac{k_Ca_C}{k_Ba_B},\quad \text{hence}$$

$$\frac{\varphi_AM_Aa_A}{\varphi_BM_Ba_B}=\frac{\varphi_AM_Aa_A}{\varphi_CM_Ca_C}\cdot\frac{\varphi_CM_Ca_C}{\varphi_BM_Ba_B}.$$

Macleod assigned *n*-octane as a standard liquid having $a=1$ to determine K_M, and with thus obtained $K_M=4.62\times10^{-6}$, he evaluated the association degrees of 28 kinds of liquid. However, the values of highly associated liquids such as *iso*-propyl, *n*-butyl, and *iso*-butyl alcohol seem to be doubtful. Macleod at first proposed a relation, $\eta x^4=$a constant[13], but replaced it two years later with the above quoted relation, $\eta=K_MMa/x$. Since A in the former relationship depends mainly upon the amount of molecular association, A being nearly unity for most of the normal

2) D. B. Macleod, *Trans. Faraday Soc.*, **20**, 348 (1924).
3) K. Drucker and R. Kassel, *Z. physik. Chem.*, **76**, 367 (1911).
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5) T. Ishikawa, This Bulletin, **4**, 5 (1929).
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9) W. Ramsay and J. Shields, *J. Chem. Soc.*, **63**, 1089 (1893); *Phil. Trans.*, A. **184**, 647 (1893); *Z. physik. Chem.*, **12**, 433 (1893).
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12) E. C. Bingham and J. P. Harrison, *Z. physik. Chem.*, **66**, 1 (1909); E. C. Bingham and L. W. Spooner, *Physics*, **4**, 387 (1933).
13) D. B. Macleod, *Trans. Faraday Soc.*, **19**, 6 (1923).

TABLE I

CASES OF EQUAL MAGNITUDE OF K AND $\varphi_2M_2/\varphi_1M_1$

Component 1	Component 2	t°C	K	$\varphi_2M_2/\varphi_1M_1$	Observers
C_2Cl_3H (0.99~1.02)	C_2Cl_3H (1.02~1.05)	25	0.40	0.389	Herz and Rathman (1913)
$C_2H_5COOC_2H_5$ (1.13~1.20)	$CH_3COOC_3H_7$ (1.16~1.21)	20 40	0.87 0.98	0.922 0.934	Unkovskaja and Volova (1925)
$C_6H_5CH_3$ (1.16~1.14)	C_6H_5Br (1.19~1.05)	20 35	0.86 0.85	0.866 0.878	Yajnik, Bhalla, Talwar and Soofi (1925)
m-$CH_3C_6H_4OH$ (1.81~1.60)	p-$CH_3C_6H_4OH$ (1.82~1.62)	25	0.90	0.910	Kendall and Beaver (1921)

TABLE II

COMPARISON OF TWO VALUES OF ASSOCIATION DEGREES DUE TO MACLEOD

Substance	x(0°C)	A	x^A	$(x)_{A=1}$	a'	a	a'/a
CH_3OH	0.1037	1.5595	0.0291	0.0580	1.99	3.20	0.62
C_2H_5OH	0.09215	1.948	0.00961	0.0450	4.68	3.75	1.25
n-C_3H_7OH	0.0333	1.3237	0.0110	0.0233	2.12	3.26	0.65
iso-C_3H_7OH	0.0559	2.104	0.00231	0.0252	10.9	4.14	2.63
n-C_4H_9OH	0.0563	2.085	0.00248	0.0248	10.0	3.77	2.65
iso-C_4H_9OH	0.0964	3.405	0.000347	0.0243	70.0	5.71	12.26

liquids, there may exist the equality: $x^A=(x)_{A=1}/a'$, where a' is the association degree when x^A can fortunately be reduced to $(x)_{A=1}$. The actual estimation of $(x)_{A=1}$ appears to be too difficult to obtain concordant values of a' with his obtained values of a, as clearly recognized from a'/a in Table II.

The present author, taking the association degrees of n-hexane and carbon tetrachloride as unity, has calculated those of 27 kinds of liquid, each being taken as a possible mean value as stated above (see Table III in which the values obtained by other investigators are also tabullated for reference).

Interpretation for the Abnormal Value of Na—K System—Quite recently Sakai[14] made experiments on the absorption spectra of mixed fused salts and led to the supposition that the great shift of absorption edge to long wave-length side with the rise of temperature may be the degradation of molecular association of component salts in the systems of $PbCl_2$—$PbBr_2$, $CdBr_2$—CdI_2, $CdCl_2$—CdI_2, and $PbCl_2$—$CdCl_2$.

Now we shall return to the pairs $PbBr_2$—$PbCl_2$, $CdCl_2$—$CdBr_2$ AgBr—AgCl, and Na—K.

For $PbBr_2$(1)—$PbCl_2$(2) system at 510°C, $K=0.33$ and

$$\frac{\varphi_2M_2}{\varphi_1M_1}=\frac{\eta_1M_2}{\eta_2M_1}=\frac{0.0354\times278.12}{0.0495\times367.04}=0.542,$$

$$\therefore\quad \frac{a_1}{a_2}=\frac{0.542}{0.33}=1.64.$$

N.B. The melting points and latent heats of fusion of $PbBr_2$ and $PbCl_2$ are 490°C and 4.530 kcal./g-mol., and 498°C and 5.136 kcal./g-mol. respectively.[15]

For $CdCl_2$(1)—$CdBr_2$(2) system at 600°C, $K=0.82$ and

$$\frac{\varphi_2M_2}{\varphi_1M_1}=\frac{0.0232\times272.24}{0.0258\times183.32}=1.348,$$

$$\therefore\quad \frac{a_1}{a_2}=\frac{1.348}{0.82}=1.64.$$

For AgBr(1)—AgCl(2) system at 500°C, $K=1.21$ and

$$\frac{\varphi_2M_2}{\varphi_1M_1}=\frac{0.0284\times143.34}{0.0207\times187.80}=1.047,$$

$$\therefore\quad \frac{a_2}{a_1}=\frac{1.21}{1.047}=1.16.$$

N.B. The melting points and latent heats of fusion of AgBr and AgCl are 430°C and 2.365 kcal./g-mol., and 455°C and 3.058 kcal./g-mol. respectively.[15]

For Na(1)—K(2) system at 103.7~192.8°C, K and $\varphi_2M_2/\varphi_1M_1$ are as follows:

°C	103.7	121.5	147.0	167.4	192.8	mean
K	2.61	2.54	2.45	2.51	2.55	2.54
$\varphi_2M_2/\varphi_1M_1$	2.724	2.678	2.638	2.599	2.581	2.644
a_1/a_2	1.043	1.054	1.077	1.035	1.012	1.04

N.B. The melting points and latent heats of fusion of Na and K are 97.7°C and 0.621 kcal/g-atom, and 63°C and 0.508 kcal./g-atom respectively[16].

14) K. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sec, (Nippon Kagaku Zassi)*, **78**, 1108 (1957).

15) Quoted from International Critical Tables, V. pp. 131—135.

16) Quoted from F. Henning, Wärmetechnische Richtwerte, pp. 14—15.

TABLE III
ASSOCIATION DEGREES OF LIQUIDS

Substance	Ramsay and Shields (16~46°C)	Traube (15°C)	Macleod (0°C)	Bingham and Spooner	This author (20~60°C)
n-C_6H_{14}	—	1.00	0.99	1.03~1.02	1.00
$CHCl_3$	0.92	1.00	1.19	1.02~1.06	1.00
CCl_4	1.01	1.00	1.12	1.09~1.00	1.00
CH_3I	—	1.30	0.90	0.98~1.05	1.00
C_2H_5I	1.01	1.19	0.92	0.99~1.04	1.24
CS_2	1.07	—	1.50	0.93~1.02	1.10 / 2.10
C_2H_5SH	1.04	—	—	1.05~1.10	1.29
CH_3COCH_3	1.26	1.53	1.66	1.28~1.31	1.74
C_6H_6	1.01	1.18 (16°C)	1.45	1.32~1.22	1.48
$C_6H_5CH_3$	—	1.08	1.15	1.16~1.14	1.40
C_6H_5Cl	1.03	1.00 (20°C)	—	1.10~1.12	1.84
$HCONH_2$	6.18(20~30°C)* / 4.85(45~60°C)*	—	—	2.00~3.40	4.93
$C_6H_5NO_2$	0.93	1.47 (20°C)	—	1.23~1.77	1.38
$C_6H_5NH_2$	1.05	1.35 (20°C)	—	1.62~2.03	2.93
C_9H_7N (Quinoline)	0.81	—	—	1.33~1.58	2.32
$C_2H_5OC_2H_5$	0.99	1.00	1.04	1.02~1.06	1.27
CH_3COOCH_3	—	1.48 (0°C)	1.35	1.23~1.33	1.99
$CH_3COOC_2H_5$	0.99	1.25	1.16	1.20~1.25	1.85
CH_3COOH	3.62 / 2.13(20°C)**	1.56	2.53	1.71~1.95	3.01
H_2O	3.44(20~30°C) / 1.64(20°C)**	3.06	—	—	6.79
CH_3OH	3.43 / 2.32(20°C)**	1.79	3.20	1.93~1.89	2.22
C_2H_5OH	2.74 / 1.65(20°C)**	1.67	3.75	1.98~1.90	2.44
n-C_3H_7OH	2.25	1.66	3.26	1.92~1.78	2.87
iso-C_3H_7OH	2.86	1.53	4.14	2.01~1.72	2.77
n-C_4H_9OH	1.94	—	3.77	1.85~1.63	2.57
iso-C_4H_9OH	1.95	1.54	5.61	1.95~1.63	2.25
C_6H_5OH	—	1.43 (20°C)	—	1.89~1.71	3.33

* W. E. S. Turner, E. W. Merry, *J. Chem. Soc.*, **1910**, 2069.
** W. Ramsay, *Z. physik. Chem.*, **15**, 111 (1894).

TABLE IV
K AND $\varphi_2M_2/\varphi_1M_1$ VALUES OF ISOMORPHIC COMPOUNDS

Component 1	Component 2	t°C	K	$\varphi_2M_2/\varphi_1M_1$
Stilbene ($C_6H_5CH{:}CHC_6H_5$)	Azobenzene ($C_6H_5N{:}NC_6H_5$)	125	0.862±0.013	1.831
Stilbene	Dibenzyl ($C_6H_5CH_2CH_2C_6H_5$)	125	0.951±0.006	2.361
Stilbene	Benzalaniline ($C_6H_5CH{:}NC_6H_5$)	125	0.902±0.009	2.516
Azobenzene	Dibenzyl	75	1.03 ±0.09	1.290
Azobenzene	Benzalaniline	75	1.03 ±0.02	1.372
Benzalaniline	Benzylaniline ($C_6H_5CH_2NHC_6H_5$)	75	0.992±0.006	1.531

TABLE V
ASSOCIATION DEGREES OF ISOMORPHIC COMPOUNDS AT 125°C

Compound	m.p. °C	Heat of fusion kcal./g-mol.[15]	Association degree at 125°C estimated	calculated from Eq. (1)	Eq. (2)
Benzylaniline	32	4.002	1.00	(1.25)	1.02
Benzalaniline	49	—	1.54	1.56	1.52
Dibenzyl	52	5.649	1.64	1.62	1.61
Azobenzene	68	5.280	2.05	2.02	2.07
Stilbene	124	7.215	4.24	4.27	(3.70)

As judged from Sakai's first and second experimental results summarized in two figures on single salts[17], the temperature variation of absorption edge of $PbBr_2$ is greater than that of $PbCl_2$, and that of $CdCl_2$ is greater than that of $CdBr_2$. These facts run parallel with the here-obtained association degrees, that is, the association degrees, of $PbBr_2$ and $CdCl_2$ are 1.6 times greater than those of $PbCl_2$ and $CdBr_2$ respectively.

Before entering into the study on Na—K system, we shall add two more systems of molten metals of different crystal forms, lead—tin and lead—bismuth[18].

For both cases, Ishikawa's formula holds strictly good (deviations are at most ±1 in the last cipher of absolute viscosity values), giving for Pb(1)—Sn(2) system $K=1.15$(400°C) and 1.03(500°C), $\varphi_2M_2/\varphi_1M_1=0.926$(400°C) and 0.897(500°C); and for Pb(1)—Bi(2) system $K=2.60$(400°C) and 1.58(500°C), $\varphi_2M_2/\varphi_1M_1=1.323$(400°C) and 1.263(500°C), whence we obtain $a_2/a_1=1.24$ (400°C) and 1.16(500°C) for the former pair, and $a_2/a_1=1.97$(400°C) and 1.25(500°C) for the latter pair.

N.B. The melting points and latent heats of fusion of lead, tin, and bismuth are 327.4°C and 1.18 kcal./g-atom, 231.9°C and 1.66 kcal./g-atom, and 271.0°C and 2.72 kcal/g-atom respectively.[16]

In regards to metals, the atomic complexity of bismuth degrades greatly from 1.97 to 1.25; that of tin degrades slightly from 1.24 to 1.16 both for 100° temperature interval, whereas sodium and potassium, judging from the constancy of a_1/a_2 throughout the temperature range, 103.7~192.8°C, may undoubtedly be monoatomic, or else greatly similar in atomic complexity against temperature change, and hence the constant, $K=2.54$ for the pair composed of these metals, is not abnormal, but is typically normal just as the pair of pentachloroethane(1)—trichloroethylene(2) ($K=1/0.40=2.5$) in Table I.

Examples for elucidating the Degradation of Molecular Complexity—The six cases of ideal mixtures[19] composed of isomorphic and greatly similar compounds in chemical constitution as shown in Table IV are those which nearly satisfy the additive law, i.e., $K=1$, but their corresponding $\varphi_2M_2/\varphi_1M_1$ takes something other than unity. This discrepancy, however, would be elucidated in the following way.

From K values of five pairs except the last, the already mentioned condition for three ideal mixtures composed of three kinds of liquids are calculated as follows:

$$0.862\times\frac{1}{0.951}\times1.03=0.933,$$

$$0.902\times\frac{1}{0.862}\times\frac{1}{1.03}=1.016.$$

These values approach nearer to unity, if we take the probable errors of K into account, and therefore the condition is fairly satisfied in spite of a wide temperature difference, 50°, taken in the viscosity measurements.

Since these isomorphic compounds have, according to the observer, equal viscosity values at the temperature of 1° above their melting points (viscosity values relative to that of water at 4°C are 1.3909±0.0037 or ±0.265% deviations from the mean), the molten state at their melting points should be in equal molecular association. Assuming then that the association degree of benzylaniline having the lowest melting point among them is unity at 75°C, the association values of benzalaniline, dibenzyl, and azobenzene have been found from the pairs at 75°C to be 1.54, 1.64, and 2.05 respectively, and by applying these values to the pairs at 125°C the association degree of stilbene has been estimated to be 4.35, 4.07, 4.30 or the mean 4.24.

17) K. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 138, 306 (1957).
18) R. Arpi, *Z. Metallographie*, **5**, 142 (1914).
19) K. Beck, *Z. physik. Chem.*, **48**, 652 (1904).

These values in the reverse order in Table V are presumably regarded to be the association degrees of any one of these compounds at temperatures of 1°, 57°, 73°, 76°, and 93° above its melting point (temperature differences of each melting point from 125°C). If it be really so, there should exist some simple functional relationship between the association values and their corresponding temperature differences. Taking logarithms of the association values, a, as ordinate and the temperature differences, Δt, as abscissas, we can easily find that a linear relaiton

$$\log a = 0.6365 - 0.00582\,\Delta t \qquad \text{(i)}$$

nearly holds except the lowest value. Next taking a as ordinate and Δt as abscissa, the following simplest relation

$$a = 3.73 - 0.0291\,\Delta t \qquad \text{(ii)}$$

holds except the highest value. Judging from these two trials, it is highly probable that the molecular association of these compounds degrades at first rapidly (logarithmically) in the neighborhood of the melting point, but then gradually with the rise of temperature.

Summary

In the previous paper on the same subject the author made an erroneous explanation on the result of Na—K system.

Comparison of Ishikawa's formula with Drucker and Kassel's formula leads to the new relation, $K = \varphi_2 M_2 a_2 / \varphi_1 M_1 a_1$, from which the association degrees of 27 kinds of liquid have been evaluated.

By the use of this relation, the abnormally high value of K of Na—K system has been proved to be normal.

Two systems of different crystal forms, Pb—Sn and Pb—Bi, and six systems composed of isomorphic compounds, benzylaniline, benzalaniline, dibenzyl, azobenzene, and stilbene are added for elucidating the degradation of atomic or molecular complexity with rise of temperature.

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Resolution of Amino Acids. I. Resolution of Racemic Phenylalanine and γ-Phenyl-α-aminobutyric Acid by Leucine Aminopeptidase

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(Received February 22, 1958)

Several methods have been described for the resolution of racemic phenylalanine[1,2] and phenylaminobutyric acid[3], but no method involving the asymmetric hydrolysis of the amides of these two racemic amino acids by aminopeptidase has yet been shown. As Smith[4] has reported that the highly active leucine aminopeptidase was prepared easily from swine kidney and found to hydrolyze L-phenylalaninamide at a moderate rate, we tried in the present work to resolve racemic phenylalaninamide and phenylaminobutyric acid amide by making use of the enzyme.

We prepared a partially purified leucine aminopeptidase of Step 4 according to Smith[4] by which phenylaminobutyric acid amide was also found to be hydrolyzed at a higher rate than that for L-phenylalaninamide. For the resolution, the initial substrate concentration was set at 0.1 mol. for DL-phenylalaninamide and 0.05 mol. for DL-phenylaminobutyric acid amide, the course of hydrolysis was followed by measurements of evolved ammonia, and the digest was allowed to stand beyond the point at which analysis reveals the theoretical 50% hydrolysis. In the course of the digestion of phenylaminobutyric

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1) J. P. Greenstein, *Advances in Protein Chem.*, **9**, 121 (1954).

2) K. Michi and H. Tsuda, *J. Jap. Biochem. Soc.*, (*Seikagaku*) **29**, 646 (1957).

3) V. du Vigneaud and O. J. Irish, *J. Biol. Chem.*, **122**, 349 (1938).

4) E. L. Smith, "Methods in Enzymology", vol. 2, edited by S. P. Colowick and N. O. Kaplan, Academic Press Inc., New York, (1956), p. 88; D. H. Spackman, E. L. Smith and D. M. Brown, *J. Biol. Chem.*, **212**, 255 (1955).

acid amide, the L-isomer which is remarkably insoluble in water was partly precipitated.

The products of the reaction were separated in two ways: namely, by differential solubility and the use of ion-exchange resin. It was found that the former way is conveniently applied for the separation of the products from DL-phenylaminobutyric acid amide and the latter way is for that of DL-phenylalaninamide.

For the resolution of phenylaminobutyric acid, only one method has been reported by du Vigneaud and Irish[3], which is based on the fractional crystallization of the brucine salt of the racemic formyl derivative. They assigned the L optical configuration to the isomer of $[\alpha]_D^{30}$ +48.8° (in 1 N hydrochloric acid) according to the Lutz-Jirgensons rule and on the basis of the animal feeding experiment. Since the enzyme employed here was completely inactive toward D-leucinamide, and since no D-leucine aminopeptidases have yet been found in animal tissues, it was assumed that the susceptible isomer was L in optical configuration. The digest contained, therefore, L-amino acid and D-amino acid amide at the end of the incubation. L-Phenylaminobutyric acid obtained here possessed $[\alpha]_D^9$ of +48.1° in 1 N hydrochloric acid, which coincides with the results of du Vigneaud and Irish[3].

Experimental

Preparation of leucine aminopeptidase. A partially purified enzyme solution (Step 4 of Smith) was prepared as described[4]. Table I shows the proteolytic coefficients (C_1) of L-amino acid amides. The C_1 of L-leucinamide is included for comparison. The rate of enzyme action on the amides was followed by measurement of the extent of ammonia liberation in Conway micro-diffusion vessels[5]. The rate of hydrolysis ($C_1 \times$ substrate concentration) of phenylalaninamide and phenylaminobutyric acid amide with the enzyme preparation slightly increased with increase in concentration of the substrates.

TABLE I

PROTEOLYTIC COEFFICIENT (C_1) OF AMINO ACID AMIDES BY PARTIALLY PURIFIED LEUCINE AMINOPEPTIDASE*

Substrates	C_1 at different concn. of substrates**		
	0.01 M	0.025 M	0.05 M
L-Leucinamide	5.5	3.6	2.2
DL-Phenylalaninamide	2.4	1.0	0.5
DL-Phenylaminobutyric acid amide***	8.2	3.4	2.1

* Enzyme was preincubated in 0.1 M Tris buffer of pH 8.0 with 0.008 M manganous chloride for one hour at 38°C. Assays were conducted in 0.1 M Tris buffer of pH 8.0 at 38°C with preincubated enzyme added. $C_1 = \log[100/(100-\%\text{ hydrolysis})]/(\text{min.} \times \text{mg. protein } N \text{ per ml. test solution})$.

** Concentrations of L form of substrates.

*** Crystals of L-amino acid appeared after 50~70% hydrolysis.

The effect of various manganous ion concentrations on hydrolysis of the substrates under the same conditions of the resolution was examined. In the presence of manganous ions (0.0005~0.008 M), the apparent increase of hydrolysis was observed in the case of phenylalaninamide, while little effect of the presence of manganous ions was shown with phenylaminobutyric acid amide.

Substrates. *1. DL-Phenylalaninamide hydrochloride.*—This was synthesized from DL-phenylalanine ethyl ester hydrochloride by the same procedure as that for the L form[6]; yield 95%; m. p. 234~236°C (decomp.).

Anal. Found: N, 13.80. Calcd. for $C_9H_{13}ON_2Cl$: N, 13.96%.

2. DL-γ-Phenyl-α-aminobutyric acid.—Procedure[7] Rothstein and Miller's was slightly modified, the yield being remarkably improved. After refluxing the mixture of ethyl acetamidocyanoacetate, sodium and β-phenylethyl bromide in ethanol, the precipitated salt was filtered off and a small amount of acetic acid was added as described in Rothstein and Miller's paper. The filtrate was then evaporated in vacuo to an oil which was changed to crystals by the addition of water. The crystals were collected and washed with water. A part of the crude crystals was recrystallized from ethanol-water; m. p. 116°C. This is ethyl acetamidocyanophenylbutyrate.

Anal. Found: N, 10.36. Calcd. for $C_{15}H_{18}O_3N_2$: N, 10.21%.

The main part of the crude crystals was refluxed with concentrated hydrochloric acid and turned to phenylaminobutyric acid in the usual manner; yield 66% (based on ethyl acetamidocyanoacetate); m. p. 300~302°C (decomp.). The reported melting point is 305~306°C[3].

3. DL-γ-Phenyl-α-aminobutyric acid ethyl ester hydrochloride.—DL-Phenylaminobutyric acid (81g.) was suspended in ethanol (1.5 l.), dry hydrogen chloride was introduced to saturation at room temperature, and the solution was refluxed for one hour. Removal of the solvent in vacuo and treatment of the residue with dry ether yielded crystals. This was recrystallized from ethanol-ether; yield 98 g. (88%); m. p. 135~136°C.

Anal. Found: N, 5.69. Calcd. for $C_{12}H_{18}O_2NCl$: N, 5.75%.

4. DL-γ-Phenyl-α-aminobutyric acid amide hydrochloride.—This was prepared from DL-phenylaminobutyric acid ethyl ester hydrochloride in

5) R. B. Johnston, M. J. Mycek and J. S. Fruton, ibid. **185**, 629 (1950).
6) E. L. Smith and D. H. Spackman, ibid. **212**, 271 (1955).
7) M. Rothstein and L. L. Miller, ibid. **199**, 209 (1952).

the same way as that for the L-phenylalaninamide hydrochloride[6] and recrystallized from methanol-ether; yield 91%; m. p. 214~217°C (decomp.).

Anal. Found: N, 13.21. Calcd. for $C_{10}H_{15}ON_2Cl$: N, 13.05%.

Resolution of DL-phenylalaninamide. *A. Separation method involving ion-exchange chromatography. 1. D-Phenylalaninamide hydrochloride.*—DL-Phenylalaninamide hydrochloride (45.2 g.) was dissolved in water (1.5 l.) containing manganese chloride tetrahydrate (0.224 g.). The pH was adjusted to 7.5 with 1 N aqueous ammonia (about 180 ml.), the enzyme solution containing the equivalent of 2.25 mg. of protein nitrogen was added, and the volume was made up to 2.25 l. After forty hours' incubation at 38°C, the results of ammonia determination indicated complete hydrolysis of the susceptible L-isomer, when the pH of solution was found to be 8.5. The course of a typical hydrolysis is shown in Fig. 1.

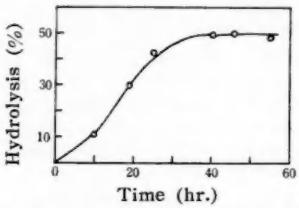

Fig. 1. Time-course of hydrolysis of DL-phenylalaninamide.

The solution that remained clear was passed through a column of Amberlite IRA-400* in the alkaline phase (5 cm.×40 cm.) and water (8 l.) was added to the top of the column. Detection of the amide and ammonia in the fractions was accomplished by means of the Nessler's reagent or the ninhydrin spot test on paper. The fractions were combined and evaporated to dryness in vacuo. The evaporation was repeated several times with addition of ethanol, and the remaining oil was crystallized after being kept in a desiccator for two to three days. The crystals were dissolved in 0.5 N methanolic hydrochloric acid (225 ml.)**. The solution was evaporated to small volume and ether was added. The resulting crystals were collected and recrystallized from methanol-ether; yield 18.6 g. (82%); m. p. 235~237°C (decomp.); $[\alpha]_D^{12}$ −20.4° (c 2, in water).

Anal. Found: C, 53.65; H, 6.55; N, 13.81. Calcd. for $C_9H_{13}ON_2Cl$: C, 53.87; H, 6.53; N, 13.96%.

The reported values for L-phenylalaninamide hydrochloride are $[\alpha]_D^{25}$ +20.7° and m. p. 246°C[6].

2. L-Phenylalanine.—Elution of the L-amino acid from the column was accomplished with 2 N hydrochloric acid (10 l.). Detection of the fractions was accomplished by means of the paper chromatography. The fractions were evaporated to dryness in vacuo three times to remove the excess of hydrochloric acid. The residue was dissolved in water and neutralized with triethylamine. The crystals were recrystallized from hot water-ethanol; yield 17.3 g. (93%); m. p. 270~273°C (decomp.); $[\alpha]_D^{12}$ −34.1° (c 2, in water).

Anal. Found: C, 65.61; H, 6.59; N, 8.26. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48%.

The reported values are $[\alpha]_D^{25}$ −33.35° and m. p. 273~275°C[8].

3. D-Phenylalanine.—D-Phenylalaninamide hydrochloride (4.0 g.) was refluxed with 2 N hydrochloric acid (60 ml.) for five hours and D-phenylalanine was obtained in the usual manner; yield 3.0 g. (91%); m. p. 271~274°C (decomp.); $[\alpha]_D^{9}$ +33.8° (c 2, in water).

Anal. Found: N, 8.41. Calcd. for $C_9H_{11}O_2H$: N, 8.48%.

B. Separation method involving fractional crystallization. 1. L-Phenylalanine.—DL-Phenylalaninamide was resolved as described above. The incubation mixture was evaporated to a small volume and ethanol was added. The resulting crystals were collected and recrystallized from hot water-ethanol; yield 51~55%; $[\alpha]_D^{12}$ −35.1° (c 2, in water).

Anal. Found: N, 8.31. Calcd. for $C_9H_{11}O_2N$: N, 8.48%.

2. D-Phenylalaninamide hydrochloride.—The filtrate and washings from L-amino acid were evaporated to dryness in vacuo and the residue was treated as described later in the preparation of D-phenylaminobutyric acid amide hydrochloride; yield 77~81%; m. p. 234~237°C (decomp.); $[\alpha]_D^{12}$ −20.1° (c 2, in water).

Anal. Found: N, 14.21. Calcd. for $C_9H_{13}ON_2Cl$: N, 13.96%.

Resolution of DL-γ-phenyl-α-aminobutyric acid amide. *1. L-γ-Phenyl-α-aminobutyric acid.*—To DL-phenylaminobutyric acid amide hydrochloride (64.5 g.) dissolved in water, pH being brought to 7.5 with aqueous ammonia, was added the enzyme equivalent to 0.9 mg. of nitrogen. The mixture was made up to 6 l. with water and incubated at 38°C. After about thirty hours beautiful crystals appeared, and after another twenty hours the mixture was cooled for the complete precipitation. The crystals were collected and washed thoroughly with cold water; yield 15.6 g. The filtrate and washings were combined, the additional enzyme equivalent to 0.6 mg. of nitrogen was introduced, and the volume was adjusted to 9 l. After another twenty hours' incubation at 38°C, the results of ammonia determinations indicated complete hydrolysis, no crystals appearing this time. The incubation was continued for another fifteen hours. The course of hydrolysis is shown in Fig. 2. The solution was evaporated to about 150 ml., and the

* In another run, Amberlite IRC-50 in the acid phase, a weak cation-exchange resin, was applied to the separation, but the eluate of the digest contained total amount of L-amino acid with parts of D-amide and ammonia even though a large amount of resin was used.

** The paper chromatography of this solution showed only one spot by means of the ninhydrin test with several solvent systems.

8) S. Sakurai, *J. Biochem.*, **43**, 851 (1956).

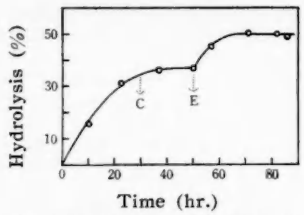

Fig. 2. Time-course of hydrolysis of DL-phenylaminobutyric acid amide. At the point of C, crystals appeared. At the point of E, additional enzyme was added.

resulting crystals were collected; yield 10.5 g. (combined filtrate and washings saved for the D-amide). The combined crystals (26.1 g.) were recrystallized from hot dilute hydrochloric acid-aqueous ammonia; yield 24.5 g. (91%); m. p. 310~313°C (decomp.); $[\alpha]_D^9$ +48.1° (c 1, in 1 N hydrochloric acid).

Anal. Found: C, 66.84; H, 7.44; N, 7.72. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82%.

The reported value is $[\alpha]_D^{30}$ +48.8°[3].

2. D-γ-Phenyl-α-aminobutyric acid amide hydrochloride.—The combined filtrate and washings from L-amino acid were evaporated to dryness in vacuo and 5 N sodium hydroxide (75 ml.) was added thereto under cooling. The solution was extracted three times with 3 l. (total volume) of chlorofom. Chloroform solution was dried over sodium sulfate and evaporated to dryness in vacuo. The oily residue was dissolved in 0.5 N methanolic hydrochloric acid (300 ml.), solution was evaporated to small volume, and ether was added. The resulting crystals were collected and recrystallized from methanol-ether; yield 27.2 g. (84%); m. p. 253~254°C (decomp.); $[\alpha]_D^9$ −23.7° (c 2, in water).

Anal. Found: C, 56.12; H, 7.21; N, 12.96. Calcd. for $C_{10}H_{13}ON_2Cl$: C, 55.94; H, 7.04; N, 13.05%.

3. D-γ-Phenyl-α-aminobutyric acid. — This was obtained from D-amide hydrochloride by the same procedure as that for D-phenylalanine; yield 96%; m. p. 308~311°C (decomp.); $[\alpha]_D^9$ −48.7° (c 1, in 1 N hydrochloric acid).

Anal. Found: N, 7.86. Calcd. for $C_{10}H_{13}O_2N$: N, 7.82%.

The reported values are $[\alpha]_D^{30}$ −47.0° and m. p. 323~325°C[3].

Summary

DL-Phenylalaninamide and DL-phenylaminobutyric acid amide were resolved to L-amino acids and D-amino acid amides by the partially purified leucine aminopeptidase preparation.

The products in the digests were separated conveniently by the use of ion-exchange resin, Amberlite IRA-400, in the case of DL-phenylalaninamide, while by the differential solubility in the case of DL-phenylaminobutyric acid amide.

The parts of D-amino acid amide hydrochlorides obtained were changed to D-amino acids by acid hydrolysis.

We wish to express our thanks to Professors S. Shibuya and Y. Yamamura of Kyushu University for their continued interest in this work.

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The Study of the Adsorption of Detergents at a Solution-Air Interface by Radiotracer Method. I. Adsorption Isotherm for the Solution of Sodium Alkyl Sulfates

By Ryohei MATUURA, Hideo KIMIZUKA, Shigeru MIYAMOTO and Ryosuke SHIMOZAWA

(Received February 6, 1958)

The surface tension lowering properties of detergent solutions are well known and, of course, associated with the adsorption of the detergent at the solution-air interface. The adsorption isotherm is usually discussed on the basis of the Gibbs adsorption equation. However, the Gibbs equation is an ideal, limited equation and it is a problem whether the equation is actually valid for the adsorption of the surface active electrolytes. In the case of an anionic detergent, RNa, the Gibbs

equation may be written as

$$d\gamma = -RT\Gamma_{Na^+} d\ln C_{Na^+} - RT\Gamma_{R^-} d\ln C_{R^-} - RT\Gamma_{H^+} d\ln C_{H^+} \quad (1)$$

where γ is the surface tension of the solution; Γ_{Na^+}, Γ_{R^-} and Γ_{H^+} are amounts of adsorption of sodium ion, detergent anion and hydrogen ion, respectively; and C_{Na^+}, C_{R^-} and C_{H^+} are concentrations of each specified ion. When the concentration of hydrogen ion is kept constant, the equation may be

$$d\gamma = -RT\Gamma_{Na^+} d\ln C_{Na^+} - RT\Gamma_{R^-} d\ln C_{R^-} \quad (2)$$

Without excessive salts or alkali and with a small concentration of the detergent, assuming that $\Gamma_{Na^+}=0$, $\Gamma_{H^+}=\Gamma_{R^-}=\Gamma_{RH}$ and $C_{Na^+}=C_{R^-}=C_{NaR}$, the Eq. 2 becomes

$$\Gamma_{RH} = -\frac{1}{RT}\frac{d\gamma}{d\ln C_{RNa}}. \quad (3)$$

As the concentration of the detergent becomes higher, hydrogen ion may be replaced by sodium ion in the surface layer; hence, assuming that $\Gamma_{H^+}=0$, $\Gamma_{Na^+}=\Gamma_{R^-}=\Gamma_{NaR}$ and $C_{Na^+}=C_{R^-}=C_{NaR}$, the Eq. 2 results in

$$\Gamma_{NaR} = -\frac{1}{2RT}\frac{d\gamma}{d\ln C_{NaR}}. \quad (4)$$

In discussing on the basis of the Gibbs equation the adsorption of the detergent solution without excess salts or alkali, either Eq. 3 or Eq. 4 should be applied if either of the above assumption is satisfied. The problem is to measure the adsorbed amount directly and to compare the result with that calculated from the surface tension data using Eq. 3 or Eq. 4.

Recently the possibility of using radiotracers for the direct measurement of adsorption of detergents at the solution-air interface was developed by Dixon et al.[1], Aniansson and Lamm[2] and Hutchinson[3]. The method in general consists, though in detail some differences exist among the authors, in measuring the difference between radioactivity of tagged surface active agents in the surface adsorbed layer plus bulk solution and that in bulk solution alone. Since then, the method has actually been applied by some authors to the adsorption of respective detergent from the solutions of di-*n*-octyl sodium sulfosuccinate (Aerosol OTN)[4], potassium palmitate[5] and sodium dodecyl sulfate (abbreviated as SDS)[6-8]. The method has proved very successful for the study of adsorption of a detergent from mixtures, for example, the adsorption of Aerosol OTN from the solution of mixture of Aerosol OTN and Aerosol OT (di-2-ethylhexyl sodium sulfosuccinate) has been measured by Judson et al.[9] by tagging Aerosol OTN. Similar measurements have been made on the adsorption of sodium hexadecyl sulfate (abbreviated as SHS)[10,11] and of sodium tetradecyl sulfate (abbreviated as STS)[12] both in the presence of excess SDS, by tagging the former detergents. Nilsson has measured the adsorption of tritiated SDS and dodecanol in the presence of STS and SDS respectively[8].

The radiotracer method has also been applied to the investigation of gegen-ion adsorption from the detergent solutions, as, for example, the adsorption of the sulfate ion in solutions of some cationic, anionic and non-ionic surface active agents[13,14] and of sodium ion in solutions of SDS[3] and Aerosol OTN[15]. Further, the co-adsorption of metal ions with surface active agents has been studied by Aniansson and Steiger by making use of α-recoil atoms[16,17].

All these works have given us some interesting information which could not have been directly obtained before, as to the nature of the adsorption of detergents at the solution-air interface. Especially the validity of the Gibbs adsorption equation has been checked by a couple of authors. Salley et al.[4], Roe and Brass[5] and Ruyssen[6] obtained in the case of Aerosol OTN, potassium palmitate and SDS, respectively, the results that the adsorption

1) J. K. Dixon, A. J. Weith, Jr., A. A. Argyle and D. J. Salley, *Nature*, **163**, 845 (1949).
2) G. Aniansson and O. Lamm, ibid. **165**, 357 (1950).
3) E. Hutchinson, *J. Colloid Sci.*, **4**, 599 (1949).
4) D. J. Salley, A. J. Weith, Jr., A. A. Argyle and J. K. Dixon, *Proc. Roy. Soc.* (London), **A203**, 42 (1950).
5) C. P. Roe and P. D. Brass, *J. Am. Chem. Soc.*, **76**, 4703 (1954).
6) R. Ruyssen, *Bull. soc. chim. Belges*, **62**, 97 (1953).
7) R. Ruyssen and J. Maebe, *Mededel. Koninkl. Vlamm. Acad. Wetenschap, Belg. Kl. Wetenschap.*, **15**, No. 4, 15 (1953).
8) G. Nilsson, *J. Phys. Chem.*, **61**, 1135 (1957).
9) C. M. Judson, A. A. Argle, J. K. Dixon and D. J. Salley, *J. Chem. Phys.*, **18**, 1302 (1950).
10) G. Aniansson, *J. Phys. Chem.*, **55**, 1286 (1951).
11) R. Loos, *Mededel. Koninkl. Vlamm. Acad. Wetenschap, Belg. Kl. Wetenschap.*, **13**, 3 (1951).
12) G. Nilsson and O. Lamm, *Acta Chem. Scand.*, **6**, 1175 (1952).
13) C. M. Judson, A. A. Argyle, J. K. Dixon and D. J. Salley, *J. Chem. Phys.*, **19**, 378 (1951).
14) C. M. Judson, A. A. Lerew, J. K. Dixon and D. J. Salley, *J. Phys. Chem.*, **57**, 916 (1953).
15) C. M. Judson, A. A. Lerew, J. K. Dixon and D. J. Salley, *J. Chem. Phys.*, **20**, 519 (1952).
16) G. Aniansson and N. H. Steiger, ibid. **21**, 1299 (1953).
17) N. H. Steiger and G. Aniansson, *J. Phys. Chem.*, **58**, 228 (1954).

of the detergent at the solution-air interface takes place in accordance with the Eq. 3, provided the solution is dilute. However, the problem has not been treated for a series of surface active agents which have a similar structure but different surface activity. The investigation of the adsorption isotherm of various detergents at the solution-air interface in relation to their surface activity is an important problem in elucidating the nature of surface active agents. So we started to study the problem with application of the radiotracer method to the adsorption of a series of sodium alkyl sulfates at the solution-air interface. The present paper describes the results of the study of the adsorption isotherm for the aqueous solutions of SDS, STS and SHS.

Experimental

Materials.—The alkyl sulfates used were synthesized from corresponding fatty alcohols and concentrated sulfuric acid according to the method written in the text of Sisley[18]. The monoester was neutralized with alkali. The sodium alkyl sulfate thus produced was extracted several times with butanol[19]. By heating the butanol extract, water was removed, and the precipitated inorganic salts were separated from the solution by filtration. Then the sodium alkyl sulfate was recrystallized from the filtrate. The crystal was washed with a large amount of ether several times to remove unsulfated alcohol[20]. The result of elementary analysis verified the purity of the sodium alkyl sulfates within an experimental error. The surface tension-concentration curves for three detergents are shown in Fig. 8, which shows no minima and the values of cmc observed are in good agreement with those in literature[21].

Pure fatty alcohols were prepared by fractional distillation of commercial ones in vacuum, followed by redistillation of the fraction with conditions as shown in Table I.

TABLE I
CONDITIONS FOR THE DISTILLATION AND THE MELTING POINT OF ALCOHOLS

Alcohol	Pressure (mmHg)	Distillation temp. (°C)	m. p. (°C)
Dodecyl alcohol	20	149.6~149.8	23.5~24.5
Tetradecyl alcohol	15	167~168	37.5~38.5
Hexadecyl alcohol	17	192~193	48.5~49.5

Butanol and ether used for extraction and recrystallization were purified by redistillation of pure commercial ones, and concentrated sulfuric acid and alkali were extra pure reagents.

The sulfur-35 was obtained from the Radiochemical Center, England, as a carrier-free sodium sulfate solution. It was converted into sulfuric acid by ion-exchange resin and was isotopically diluted by a small amount of sulfuric acid. This was concentrated and used for synthesis of radioactive sodium alkyl sulfates in the manner as stated above. The specific radioactivity of the labeled sodium alkyl sulfates thus prepared was ca. 10 mc. per millimole for SDS and SHS and 2 mc. per millimole for STS.

Method.—The procedure used for measurement of surface excess of a radioactive detergent in aqueous solutions was essentially similar to that described by Aniansson[10]. The apparatus used in the present experiment is shown in Fig. 1. A lucite cuve A, 5.6 cm. in inner diameter and 0.2 cm. in depth, filled exactly to the brim with the radioactive solution, is fitted exactly to the brass table B, 5.6 cm. in diameter, as shown in the figure. The thickness of the wall of A was all 0.2 cm. The Geiger-Müller tube C (GM-132, an end window type of special use for soft β-ray) is supported by a brass cylinder D with an arm E which is fixed to a universal stand. This enables us to move the Geiger-Müller tube up and down precisely. A brass ring F, 6.0 cm. in inner diameter which is identical with the outer diameter of the cuve A, is fixed to D so that tight fitting of the arrangement and reproducibility of the geometric condition can be realized with ease. The distance between the surface of the solution and the Geiger-Müller tube window is 0.15 cm. This small distance enables us to give a low gas volume over the surface. Since the counting of the radioactive sulfuric acid solution was shown to be constant within an experimental error, 5%, over a period of several hours, the evaporation effect may be ignored during the time interval of the present experiment. The whole arrangement was set in an air thermostat to maintain a constant temperature during the experiment. The fresh

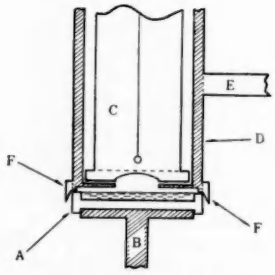

Fig. 1. The measuring apparatus.

18) J. P. Sisley. "Encyclopedia of Surface Active Agents", translated from the French and revised by P. J. Wood. Chem. Pub. Co. Inc., New York, N. Y. (1952).
19) E. E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).
20) G. D Miles and L. Shedlovsky, *J. Phys. Chem.*, **48**, 57 (1944).
21) T. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937); **34**, 372 (1938); L. Shedlovsky, J. Ross and C. W. Jacob, *J. Colloid Sci.*, **4**, 25 (1949); G. D. Miles, *J. Phys. Chem.*, **49**, 71 (1945); A. P. Brady, ibid., **53**, 56 (1949).

and plane free surface of the solution in the cuve was easily obtained by sweeping away the surface of the solution with a glass plate, about 7 cm. in width and 8 cm. in length. Both the lucite cuve and the glass plate were coated with a thin layer of paraffin to avoid wetting by the solution, and before use they were rinsed with tap water for a few hours, followed by final washing with distilled water. After the plane-free surface was formed, the Geiger-Müller tube was put down into the measuring arrangement and the intensity of radiation from the solution was measured.

The surface excess, Γ (in mole per cm^2), is calculated according to the equation

$$\Gamma = \frac{I_d - I_i}{SA}, \qquad (5)$$

where I_d is the intensity (count per min.) of radiation due to the detergent solution; I_i, that (count per min.) due to the sulfuric acid solution which is the same in both specific activity and molar concentration as the detergent solution; S, the specific activity of the detergent in count per min. per mole, and A, the surface area of the solution in cm^2.

Of these quantities, S was obtained by means of the procedure as reported by Aniansson[10]. A solution of sodium alkyl sulfate was used for the determination of S. Evaporating about 2×10^{-3} cc. of a solution of radioactive sodium alkyl sulfate dropped as a point at the center of a polished lucite plate, it was then placed in the same position as the surface of the solution under the Geiger-Müller tube and counted. The volume of the dropped solution was accurately known by using a micropipette. The lucite plate was used for the measurement of S to avoid the error resulting from the difference in back-scattering effect of water and the material of the plate[10]. Sodium alkyl sulfate dropped was 6×10^{-7} g., so that the error due to the self-absorption could be negligible. The plate was placed at the same distance from the window as the solution surface. First the point source was located at the center line of the Geiger-Müller tube and the radiation was counted (S_0). Then the plate was moved horizontally so that the point source would have a distance r from the center line and counted (S_r). The relative counting efficiency η_r may be given by S_r/S_0. In Fig. 2 the $\eta_r \sim r$ curve is plotted. Now the overall counting efficiency, η, relative to that of the center can be computed by the following equation

$$\eta = \frac{\int_0^R 2\pi r \eta_r dr}{\int_0^R 2\pi r dr}, \qquad (6)$$

where R is the radius of the surface of the solution, 2.8 cm. in the present apparatus. The value of η can be determined by graphical integration using the Fig. 2. It was found that η was 0.2237 in the present experiment. The specific activity S is given by $S_0\eta$. The values of S thus calculated for the three detergents were 7.730×10^{10} counts per min. per mole for SDS, 3.075×10^{10} counts per min. per mole for STS and 10.96×10^{10} counts per min. per mole for SHS at the given geometry in the present experiment. In Fig. 3 I_i is plotted as a function of the concentration of sulfuric acid used for the determination of I_i. This figure shows that over a range of concentration studied I_i can be expressed by an equation

$$I_i = I_0 C, \qquad (7)$$

where C is the concentration of sulfuric acid and I_0 is the intensity of radiation due to 1 M sulfuric acid. Using the relation I_i of sulfuric acid of any concentration can be obtained.

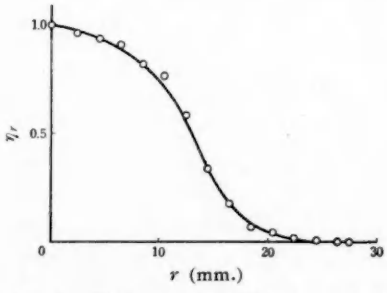

Fig. 2. The counting efficiency relative to that of the center.

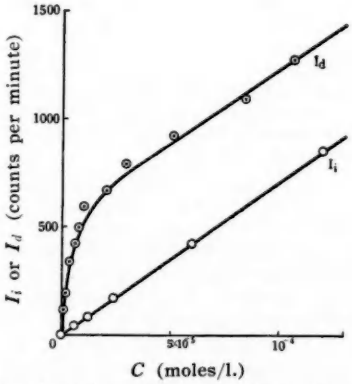

Fig. 3. The surface counts vs. concentration curves. I_i, sulfuric acid solution and, I_d, SHS solution, 28±1°C.

I_d for SHS, as an example, is also shown in Fig. 3, for comparison with I_i, as a function of the concentration of the detergent solution. Since the surface adsorption of the detergent increases with time, I_d is a function of time. I_d plotted in Fig. 3 is the value after the adsorption equilibrium has been attained. Using this figure, $I_d - I_i$ for the same concentration is read off easily and then, knowing S as stated above, the surface excess Γ can be calculated by the Eq. 5. The

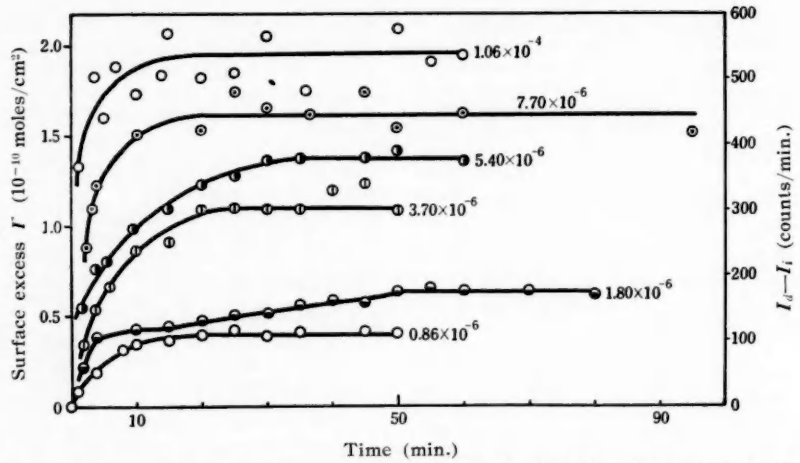

Fig. 4. Surface excess vs. time curves of SHS solution, 28±1°C. Numericals in this figure show the concentration (moles/l.) of the detergent.

same treatment can be done for the other detergents. In this case $I_d - I_i$ should be considerably greater than the statistical error of the value of I_i or I_d; otherwise the reliable value of the surface excess could not be obtained. As the concentration of the detergent solution becoms higher, the ambiguity of this source is introduced and the measurement of an accurate value of the surface excess becomes increasingly difficult. Actually in the case of SDS solution this was the case, and no data of sufficient accuracy could be obtained for this detergent at higher concentrations.

The surface tension of the detergent solution was measured by the Wilhelmy plate method. The plate was of a thin glass and mounted on a Langmuir trough assembly.

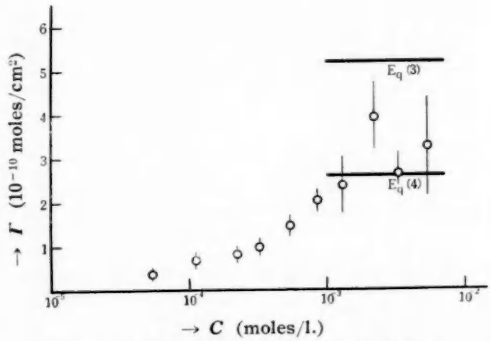

Fig. 5. Surface excess vs. concentration of SDS. 28±1°C. Full lines represent calculated relations from $\gamma \sim \log C$ curves by using Eq. 3 and Eq. 4 at 28°C.

Results and Discussion

The surface adsorption of the sodium alkyl sulfates studied in the present experiment reached the equilibrium within about an hour in every case. As an example, the surface excess of SHS is plotted against time in Fig. 4. The equilibrium is reached faster, as the concentration of the solution is higher.

The equilibrium surface excess is plotted against logarithmic concentration for SDS, STS and SHS solutions in Figs. 5, 6 and 7, respectively. The results of the measurement of Γ at different temperatures are also plotted in these figures, which indicate that the effect of temperature is not so appreciable over the range studied in the present experiment. It is seen from these figures that the surface excess has a tendency of taking a saturation value below cmc for every detergent solution.

The surface tension *vs.* logarithmic concentration data on aqueous solutions of sodium alkyl sulfates are represented graphically in Fig. 8, in which surface tension observed are those of the surface of the solution aged for an hour. It is shown that an approximately linear relation exists between γ and $\log C$ below cmc for each detergent solution. The linear portion of the $\gamma \sim \log C$ relation corresponds, although approximately, to the saturation of the surface excess obtained in the present experiment. The values of Γ calculated for this region by using Eq. 3 and Eq. 4 are shown in Figs. 5—7 for the three detergents studied. It is seen that the experimental data lie between

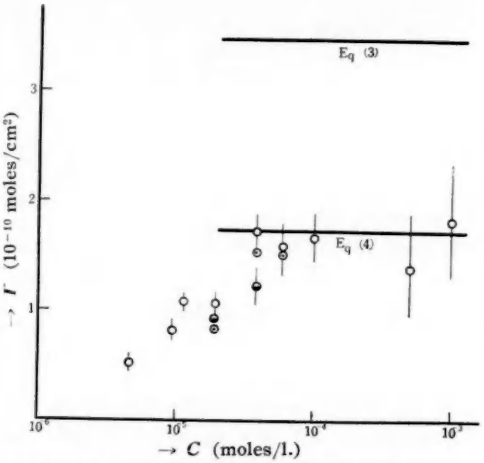

Fig. 6. Surface excess vs. concentration of STS. ○ 28±1°C; ⊙ 40±1°C; ◒ 22±1°C. Full lines represent calculated relations from $\gamma \sim \log C$ curves by using Eq. 3 and Eq. 4 at 28°C.

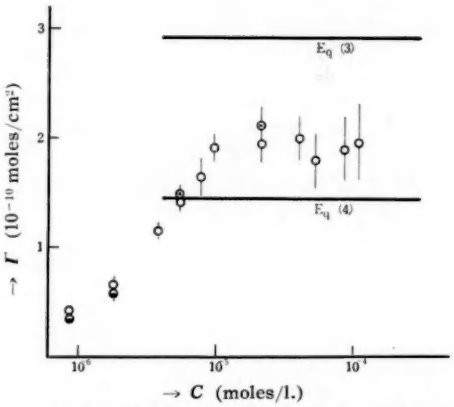

Fig. 7. Surface excess vs. concentration of SHS. ○ 28±1°C; ⊙ 40±1°C; ◒ 22±1°C. Full lines represent calculated relations from $\gamma \sim \log C$ curves by using Eq. (3) and Eq. (4) at 28°C.

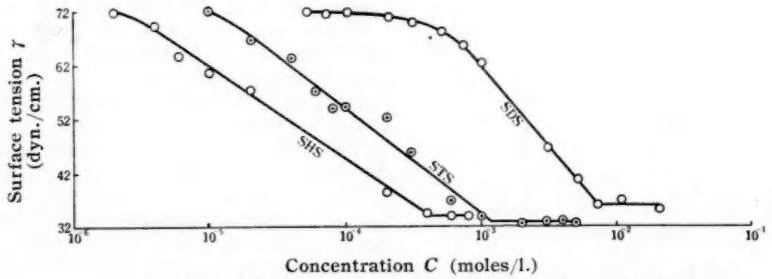

Fig. 8. Surface tension vs. concentration curves, 28±1°C.

the values of Eq. 3 and those of Eq. 4. It is to be noticed that Eq. 3 and Eq. 4 are ideal equations which are valid only if the conditions assumed in the derivation of each equation are perfectly fulfilled. The present results may show that the conditions are not so complete as to permit strict application of Eq. 3 or Eq. 4. It could be said, however, that, as a whole, the experimental points are near the values of Eq. 4 rather than those of Eq. 3 over the concentration range near cmc. Further discussion and the definite conclusion will be postponed until the accuracy of the measurements of both adsorption and surface tension at higher concentration region is improved much more.

By comparing the data of adsorption of three detergents, it is evident that the bulk concentration corresponding to the same surface excess, below the saturation of the adsorption, is lowered as the chain length of the detergent molecule increases. This is what should be expected from the surface tension lowering properties of the three detergents as shown in Fig. 8.

Summary

The adsorption of the three alkyl sulfates, SDS, STS and SHS, at the solution-air interface has been measured directly by means of the radiotracer method. It has been proved that the surface adsorption increases with increase in the concentration and has a tendency to be saturated

at concentrations near cmc for each detergent solution. The results have shown that the adsorption increases with increasing chain length. The Gibbs adsorption equation has been cheked and discussed.

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*On the Nature of the Red Adduct of Styrene with Sodium**

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(Received February 13, 1958)

As shown independently by Szwarc et al.[1] and by Meshitsuka and Okada[2], the red complexes or adducts formed between styrene and sodium have an interesting property as chain initiators; i. e., in some suitable solvents, the adducts produce living polymers which can grow when a monomer is added. According to Szwarc, the living polymers result from the dimerized styrene anions with both ends "living":

(A) $(:CHX—CH_2—CH_2—CHX:)^=$
$(X=C_6H_5)$

this bivalent anion is formed by dimerization of univalent monomer anions,

(A′) $(:CHX—CH_2\cdot)^-$ or

(A″) $(\cdot CHX—CH_2:)^-$

which are produced by the electron transfer process from naphthalene anions:

$$\text{Naphthalene}^- + \text{Styrene} \rightarrow \text{Naphthalene} + \text{Styrene}^-. \quad (1)$$

However, the proposed formula A as the initiator of the chain polymerization seems to lack firm experimental evidences.

Recently[3] two of the present authors found that there exist two other modifications in styrene adducts, blue and yellow, besides the familiar red one. Comparing the absorption spectra of these adducts with those of α-methylstyrene and *p*-divinylbenzene, not only as a dissolved state but also as a filmy state, they reached some conclusions as to the nature of styrene adducts. The adducts which were used in the research mentioned above were, however, slightly different from those of Szwarc et al. in two points; (a) the adducts** are prepared directly from styrene and metallic sodium immersed in solvents, and (b) the solvents may be non-polar ones, e. g., benzene and toluene as well as polar solvents hitherto reported (dimethylether, tetrahydrofuran, etc.).

In the above paper it is one of the conclusions that the adducts, which dissociate into sodium ions and such anions as shown by the structure A′ or A″, constitute one of the stable red adducts whose absorption maximum is 510 mμ as reported already[2]. It is the object of the present paper to reinforce the conclusion further with the paramagnetic resonance absorption measurement.

Experimental Method

Samples.—The apparatus, as shown in Fig. 1, is used to prepare most of the samples. The details of the operations will be omitted, as it has already been described[4]. Thus it was made possible generally to produce the pure adduct of aromatic hydrocarbons, e. g., styrene which was used in the present paper.

Measurement of the Paramagnetic Resonance Absorption.—The conventional apparatus which was constructed by Professor J. Itoh of Osaka University was used. The details of the measurement will be published elsewhere.

* The third report of "The research on the adduct of styrene with alkali metals": I., ref. 4, II., ref. 3.

1) M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956); M. Szwarc, *Nature*, **178**, 1168 (1956), etc.

2) G. Meshitsuka and Y. Okada, *Chemistry of High Polymers*, (*Kobunshikagaku*), **14**, 33, 37, 123 (1957).

3) K. Hirota, K. Kuwata, H. Togawa and S. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 602 (1958).

** According to the present method, the sample is free from other substance, when compared with the samples prepared indirectly by the electron transfer method, such as by Eq. 1.

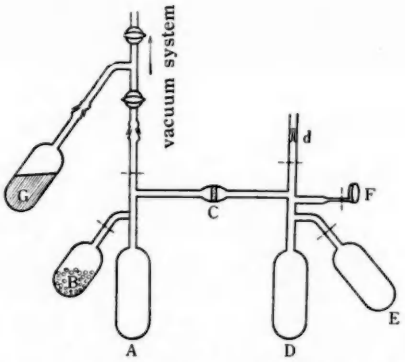

Fig. 1. Apparatus for preparation of samples
A: Reaction vessel, B: Sodium which will be vacuum-distilled into A, C: Glass filter, D: Storage vessel, E: Vessel for waste product, F: Sample cell for P. S. R. measurements, G: Styrene or toluene which will be vacuum-distilled into A, d: Breakable joint.

Results and Discussion

In the previous report[3], the structure A′ or A″ was assigned to the red adduct of styrene rather than the Szwarc's structure A from the results of absorption spectrometry. Now there will be another method of decision of this problem. Because there exists an unpaired electron in the structure A′ or A″, the paramagnetic resonance absorption may be observed if it is true, while the absorption will not be observed if the structure A is true. The measurement carried out at 9400 mc by the present writers in tetrahydrofuran solution at the concentration of 10^{-2} molar could confirm the above presumption*. One of the absorption curves is shown in Fig. 2. The Szwarc's structure A, therefore, will not be justified. In sharp contrast with naphthalene anion having seventeen or twenty-three hyperfine splitting[5], the hyperfine

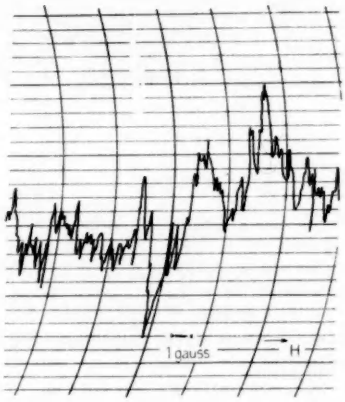

Fig. 2. Paramagnetic Resonance Absorption curve.

structure of the styrene anions seemed to consist of two lines with small intervals, but the decision which is more probable of the two structures, A′ or A″, could not be reached owing to the poor sensitivity of the apparatus. As the problem is very important in structural chemistry, further research is going on with an improved apparatus**.

Summary

Paramagnetic resonance absorption could be observed on the solution of the pure red adduct, which was prepared according to the method reported by the present writers. The adduct, therefore, produces a radical anion consisting of odd electrons by dissociation. The proposition on the structure of the red adduct in the previous report was thus confirmed.

The writers express sincere thanks to Professor Junkichi Itoh of Osaka University who made the measurement of the paramagnetic resonance absorption possible.

Faculty of Science, Osaka University
Kita-ku, Osaka

4) K. Hirota and K. Kuwata, ibid., **78**, 1421 (1957).
5) T. R. Tuttle, Jr., R. L. Ward, and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956), (17 splitting). S. I. Weissman, T. R. Tuttle and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).
6) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

* It might be necessary to refer to the Weissman's answer in discussion (*J. Phys. Chem.*, **57**, 507 (1953)) that "the paramagnetic absorption in styrene as it is undergoing polymerization initiated by metallic sodium" is not reproducible.

** Moreover the absorption may occur owing to the interaction with the proton at para-position, but such a probability will be neglected owing to the reactivity of that position.

Note added in proof: It is found that much more hyperfine structure lines can be observed in the samples made under different experimental conditions.

June 13, 1958.

Polymerization of Olefins with Trialkylboron Catalysts. II. Polymerization of Styrene

By Nobuyuki ASHIKARI

(Received February 22, 1958)

The previous work[1] in these series has shown the polymerization of vinyl chloride and acrylonitrile with trialkylboron catalysts. In the present paper the polymerization of styrene with the same catalysts is studied.

The rate of polymerization of styrene is rather smaller, in bulk system, than that of vinyl chloride or acrylonitrile. But in the emulsion system, the rate of polymerization was large and also the molecular weight of the polymer was very high.

Generally, in the polymerization of vinyl compounds with trialkylboron catalyst, it was considered that the reaction velocity and the yield of the polymer were influenced a good deal by an amount of oxygen in the reaction vessel. The degree of the influence, of course, will vary according to the sort of olefin. In this respect, the influence of oxygen in the polymerization of styrene was considered to be not very large. But, by way of precaution, the experiments in this paper were done under nitrogen stream or in a sealed tube in which the air was replaced by nitrogen. Some properties of the polymer prepared with tri-*iso*-propylboron were studied.

Experimental and Results

Preparation of the catalysts.—In a previous paper[1], the detail of the preparation of triethylboron was reported. Here, the detail of the preparation of tri-*iso*-butylboron is explained chiefly. In the cases of tri-*iso*-butyl- and tri-*iso*-propylboron, the preparations were done according to the general method, i. e., the reaction of Grignard reagent and borontrifluoride, as well as the case of triethylboron.

Triisobutylboron.—To ethereal solution of *iso*-butylmagnesiumbromide prepared by the reaction of 24 g. (1 mol.) of magnesium piece and 137 g. (1 mol.) of *iso*-butylbromide in 500 cc. three necked flask, 40 g. (0.28 mol.) of borontrifluoride etherate was dropped slowly under cooling. After the dropping was over the stirring was continued for twenty minutes.

The ethereal solution was cooled and decanted into a distilling flask. The residue consisting of magnesium halide and unchanged *iso*-butylmagnesiumbromide was treated with unhydrous ether, and the trialkylboron involved was extracted. The ethereal solution was added to the first ethereal solution, and the solvent was distilled off. The distillate of b. p. 188~195°C was collected. Thus, 34 g. of tri-*iso*-butylboron was obtained, corresponding to 56.6% yield from magnesium.

Tri-iso-propylboron. — Tri-*iso*-propylboron was prepared, by the same method, by dropping borontrifluoride etherate to isopropylmagnesiumbromide in ether.

Comparison of the rate of polymerization in bulk- and emulsion system.—The rate of polymerization in bulk- and emulsion system was compared in the following experiments. In these experiments the ratio of catalyst to monomer is constant, that is, 80 g. of monomer, and 0.296 g. of tri-*iso*-butylboron were used. Therefore, the ratio of catalyst to monomer is 0.21%.

The reactions were caused to proceed at 40°C under nitrogen stream which was purified by passing through an aqueous pyrogallol-alkali solution and drying over calcium chloride. A certain weight of monomer or a certain weight of monomer and water, was placed in a four-necked flask which was dipped in a constant-temperature bath.

A stirrer, a stopper, and a passage of nitrogen gas were connected to the flask. When the temperature of the contents reached 40°C, the catalyst was added.

After a certain interval of reaction, 10 g. of the sample was taken out from the reaction vessel, and poured into methanol. And then, the polymer contained in the sample was separated from styrene monomer, filtered, dried under reduced pressure at 50°C, and weighed. In the case of emulsion system, the sample taken out was treated with 5% aqueous sodium chloride solution, and the polymer was separated. Then, the polymer was washed fully with water, dried, and weighed.

Fig. 1 represents the relation between the conversion and the reaction time.

1) N. Ashikari, This Bulletin **31**, 229 (1958).

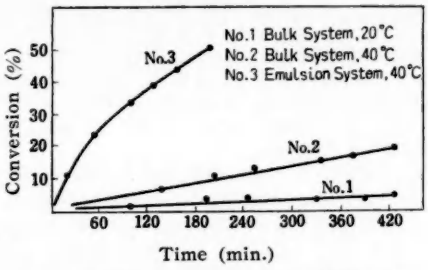

Fig. 1. The rate of polymerization in bulk- and emulsion-system.

In Fig. 1, No. 1 and No. 2 are the cases of bulk-system and No. 3 is the case of emulsion system. From Fig. 1, it is clear that the rate of polymerization in emulsion system is larger than that in bulk system. Especially, in No. 3, 80 g. of aqueous solution which contained 5% of emulsifier was used, so that the ratio of catalyst to the whole solution was very small.

The relation between the conversion and the concentration of catalyst.— A certain weight of monomer (18 g.) and a certain weight of tri-*iso*-propylboron were sealed in a nitrogen-replaced tube, and the polymerization was caused to proceed at 40°C. After ten hours reaction, each sealed tube was opened and the contents were poured into methanol. Thus, the polymer contained was separated from the monomer, filtered, dried under reduced pressure at 50°C, and weighed. The results are shown in Table 1.

TABLE I

THE RELATION BETWEEN THE CONVERSION AND THE CONCENTRATION OF CATALYST

Expt. No.	4	5	6	7	8
catalyst (%)[a]	0.0835	0.1670	0.2505	0.3340	0.4175
polymer (g.)	3.553	4.245	4.540	4.712	4.500
conversion (%)	19.74	23.58	25.22	26.18	25.00

a: catalyst/monomer mol ratio.

Molecular weight of polystyrene.— Each sample in Table 1 was dissolved in pure toluene and the viscosity was measured at 30°C with Ubbelohde viscometer. The intrinsic viscosity, $[\eta]$, was obtained from Fig. 2, in which is plotted η_{sp}/C against concentration (C), where η_{sp} represents a specific viscosity.

The molecular weight was calculated from the intrinsic viscosity with Alfrey's equation[2]; $[\eta]=0.55\times10^{-4}\,M^{0.81}$. The intrinsic viscosities and the molecular weight of the samples polymerized in bulk- and emulsion system were shown in Table II.

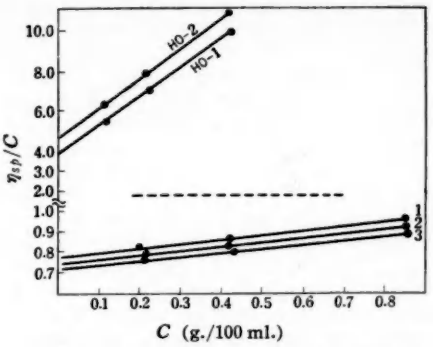

Fig. 2. Viscosity η_{sp}/C vs. C curves for polystyrene

TABLE II

THE INTRINSIC VISCOSITY AND MOLECULAR WEIGHT OF POLYSTYRENE

Exp. No.	4	5	6	HO-1	HO-2
intrinsic viscosity	0.78	0.75	0.72	3.75	4.50
mol. wt. ($\times10^{-3}$)	133	127	121	927	1160

In Fig. 2, the samples of HO-1 and HO-2 were prepared in the emulsion system. In the case of HO-1, 18 g. of monomer, 0.07 g. of tri-*iso*-butylboron, and 18 g. of aqueous solution containing 5% emulsifier were sealed in a glass tube. The reaction was caused to proceed at 40°C for five hours. The polymer was treated by the same method as mentioned on p. 540. Thus, 14 g. of the polymer was obtained. The conversion is 77%.

Similarly, in the case of HO-2, 25 g. of monomer, 0.1 g. of tri-*iso*-butylboron, and 25 g. of aqueous solution containing 5% emulsifier were used. Other conditions, i. e., temperature, time, and treatment of the polymer, were the same as in the case of HO-1. Thus, 18 g. of the polymer was obtained (72% conversion).

Generally, the molecular weight of the polymer prepared in a bulk system was $1\sim2\times10^5$, and in the case of emulsion system, the molecular weight was $1\sim2\times10^6$.

Properties of polystyrene polymerized with tri-*iso*-propylboron in bulk system.

2) T. Alfrey and A. Bartovics, *J. Am. Chem. Soc.*, **65**, 2319 (1943).

—Some properties of polystyrene polymerized with tri-*iso*-propylboron were studied.

The infrared spectra. — The infra-red spectrum of the polymer was compared with that of a polymer prepared with the ordinary catalyst such as radical type. Each film of which the thickness was about 0.01 mm. was prepared by evaporation of toluene used as a solvent of the polymer on a glass plate floated on mercury. The infrared spectrum of the polymer prepared with this catalyst almost exactly resembles that of ordinary polymer, so that only one spectrum is shown in Fig. 3.

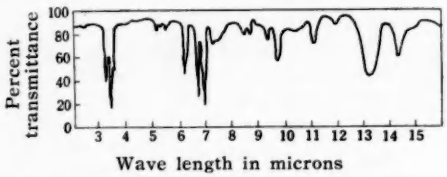

Fig. 3. Infrared spectrum of polystyrene prepared with tri-*iso*-propylboron in bulk system.

X-ray diffraction patterns.—The X-ray diffraction patterns of two samples, i. e., the ordinary polymer and the polymer prepared with this catalyst, were compared as well as the case of infra-red spectra. The specimens having 3 mm. of thickness were made by press at 150°C for ten minutes. Fig. 4-1 is a pattern of ordinary polymer and Fig 4-2 is that of the polymer described in this paper.

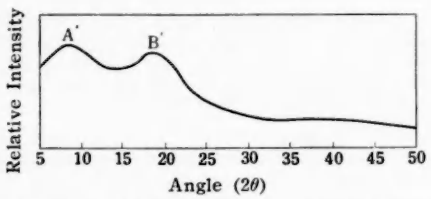

Fig. 4-1. Diffraction pattern of polystyrene prepared with peroxide catalyst.

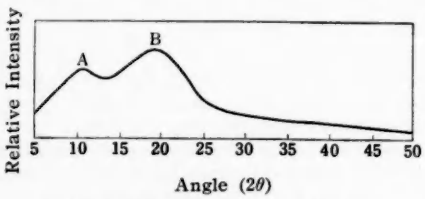

Fig. 4-2. Diffraction pattern of polystyrene prepared with tri-*iso*-propylboron.

Figs. 4-1 and 4-2 represent relative values. From these patterns, it is obvious that the relative intensities between peak A and B in Fig. 4-2 differ from those of peak A′ and B′ in Fig. 4-1.

Solubility in methyl-ethyl-ketone. — The polymer whose molecular weight was 1.2×10^5 was treated with methyl ethyl ketone for two days at room temperature. The polymer perfectly dissolved in this solvent. If the polymer is a crystalline one, it must be insoluble[3].

Softening point.—The softening point of the polymer which was the same kind as the sample used above was measured similarly by the measuring the melting point. In this case, a small piece whose size was about 0.5 mm. × 1 mm. × 20 mm. was used instead of powder in a case measuring melting point, and the temperature of deformation of the piece was observed. The softening point was about 100°C.

Summary

Styrene was polymerized with tri-*iso*-propylboron and tri-*iso*-butylboron prepared by the reaction of Grignard reagents and borontrifluorides. In regard to the rate of polymerization in bulk- and emulsion system, that in the latter was much larger than that in the former. Moreover, in the emulsion system, a very highly polymerized product was easily obtained.

Some properties of the polymer prepared with tri-*iso*-propylboron were studied in comparison with ordinary polymer. The solubility in methyl-ethyl-ketone and the infrared spectrum closely resembled those of ordinary polymers. On the X-ray diffraction pattern, a little difference was observed. But, it is not evident whether the crystalline structure exists or not.

I wish to express my sincere thanks to Mr. H. Matsuo in this laboratory who observed the infrared spectra, and to Mr. S. Ōwaki who observed the X-ray patterns.

The Electrical Communication Laboratory
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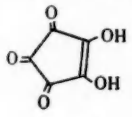
3) F. Danusso and G. Moraglis, *J. Polymer Sci.*, **24**, 161 (1957)

Structure of Croconic Acid

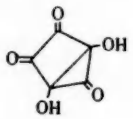
By Kiyoyuki YAMADA, Nobuhisa MIZUNO and Yoshimasa HIRATA

(Received March 3, 1958)

Croconic acid, $C_5H_2O_5$, is a yellow substance which has been known for a long time. It has a strong acidity and is sensitive to the sun light. However, there has been some ambiguity as regards its structure. So far, two structural formulas I[1] and II[2] have been forwarded; further it was suggested that there was an equilibrium involving the formula III[3] in an aqueous solution.



(I)



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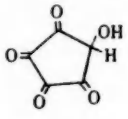


(III)

According to polarographic studies[4] of croconic acid which were done in recent years, it showed properties somewhat different from the typical enediolic compounds studied at the same time.

The properties of croconic acid were examined in order to elucidate its structure, and during the course of studies many interesting observations were obtained. Its ultraviolet spectrum differed from that expected from either structure I or II, the infrared spectrum showed a strong hydrogen bond, and its dipole moment was unusually large.

Methylation.—Since the two hydrogen atoms would naturally be expected to play a unique and important role in the characteristic properties of this acid, a methylation was first carried out. Treatment of the silver salt of the acid with methyl iodide yielded the dimethyl derivative, $C_5O_5(CH_3)_2$.

Ultraviolet spectrum.—Figs. 1—4 show the ultraviolet spectra of the croconic acid and dimethyl croconate. The solvent and the pH of the solution exert a strong influence on the spectra of croconic acid.

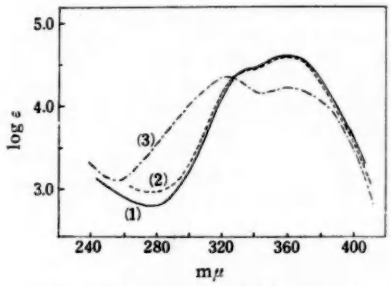


Fig. 1. Croconic acid in water.
(1): neutral; (2): 0.1 N NaOH;
(3): 0.1 N HCl.

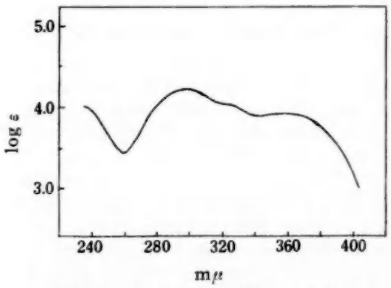


Fig. 2. Croconic acid in ethanol.

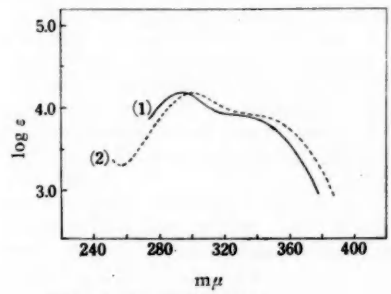
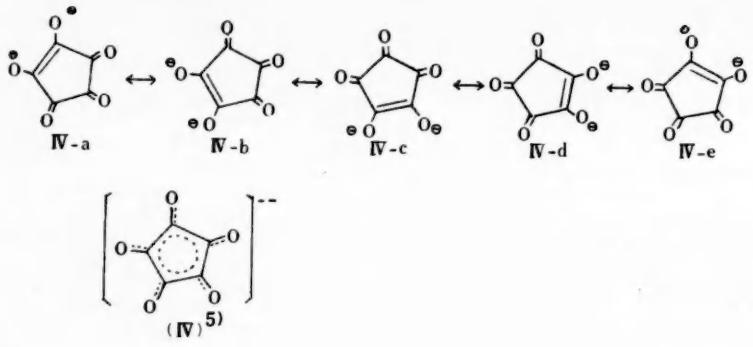


Fig. 3. Croconic acid.
(1): dioxane solution
(2): aqueous solution (9 N HCl)

In the first place, paying attention to the changes of the spectra caused by varying the solvent, we find that the spectrum in an aqueous solution substantially agrees with that in methanol,

1) R. Malachowski, *Chem. Ber.*, **71**, 2246 (1938).
2) R. Nietzki et al., ibid., **18**, 510, 1833 (1885). G. E. Carpéni, *Compt. rend.*, **206**, 601 (1938).
3) Y. Hirata et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*) **69**, 63 (1948).
4) F. Petuely et al., *Monatsh.*, **83**, 80 (1952). F. Arcamone et al., *Bull. soc. chim. France*, **1953**, 891.



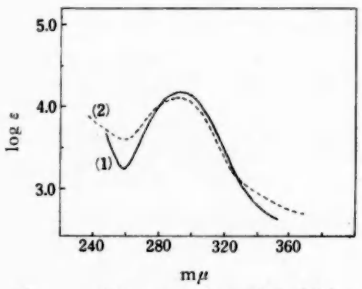


Fig. 4. (1): croconic acid in HCl gas saturated methanol
(2): dimethyl croconate in methanol

but that in ethanol there appears a new absorption in the short wave length region, and the intensity of the band common to aqueous and methanolic solution is lowered. Second, changes in pH lead to the following results; i.e., the spectra taken in a neutral and an alkaline solution are almost the same. On the other hand, when the solution is acidified, a new short wave length band appears. This new absorption is clearly different from the one observed in ethanol solution. Third, the two spectra taken in strong acidic aqueous solution (9 N hydrochloric acid) and in the non-polar dioxane agree with each other fairly well, but a general bathochromic shift of 8~10 mμ is apparent in the former solvent. Finally, though the spectrum of the dimethyl croconate taken in neutral methanol differed from that of the free acid taken in the same solvent, it showed a close similarity when the latter was taken in acidic methanol (compare Figs. 1 and 4).

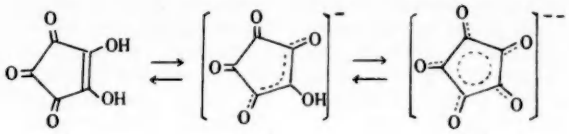
This spectral behavior may be interpreted as follows. The intensities of the absorptions in Figs. 1—3, are strong enough to exclude the possibility that the absorptions originate from the assumed structures II or III, and, moreover, the absorptions in Figs. 1 and 2 can not be attributed to the enediolic keto form I.

At first, it may be noted that the two curves in Fig. 4, namely, the absorption of the acid in strong acidic methanol, and that of its dimethyl derivative in the neutral methanol show a close resemblance (the difference of two $\lambda_{max.}$ is 3 mμ). Then, considering the positions and the intensities, it is reasonable to conclude that these two absorptions are due to I, or, in other words, due to the chromophore of the enediolic keto structure. We next turn to the absorption maxima in the long wave length region. On account of the strong acidity of croconic acid, it should be almost completely dissociated in water or in methanol to give the dianion, the "croconate ion", which presumably exists in a highly resonating state IV[5], receiving contributions from the structures IVa to IVe. Accordingly, the absorption near 295 mμ due to structure I disappears and, instead, the characteristic absorption of the croconate ion appears around 365 mμ.

In the last place, Fig. 3 will be examined. As mentioned before, the two absorptions are quite similar except the fact that one is shifted by 8~10 mμ as compared to the other. The dipole moment[6] of the acid in dioxane supports structure I with the two hydroxyl groups lying in the plane of the five membered ring. The inference from the observation is that the acid is in an undissociated state in strongly acidic

5) The dotted lines in structure IV simply denote that the two electrons are distributed throughout the entire molecule, and certainly does not denote that the molecule is mesoionic.

6) M. Washino et al., This Bulletin, **31**, 520 (1958).



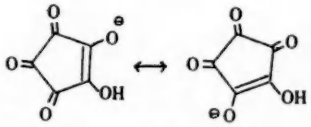
(I) (V) (IV)

aqueous solutions and takes the form of I[7]. The details of the spectra in ethanol and weakly acidic aqueous solution are illustrated in the experimental part.

Acidity.—As is apparent from the synthetic method, croconic acid is a strongly acidic compound and for this reason its purification is not easy. Since this strong acidity had already been well known qualitatively, the spectrophotometric method was applied for the measurement of pK_a.

Since two isosbestic points are present, as shown in Fig. 5, it may be inferred that two equilibrium systems exist; one is $I \rightleftarrows V$ in the low pH range, and the other is $V \rightleftarrows IV$ in the high pH range.

But from the facts that the first isosbestic point (305 mμ) is incomplete and that there exist several absorption curves at intermediate pH's which deviate from both points, it can be deduced that the dissociations do not proceed stepwise and that the croconate ion IV · is formed already in the range of low pH. The nature of the monoanion V will be considered next. The monoanion as well as the dianion is stabilized by resonance (Va, Vb); however, the extent of stabilization is smaller with the monoanion.



V-a V-b

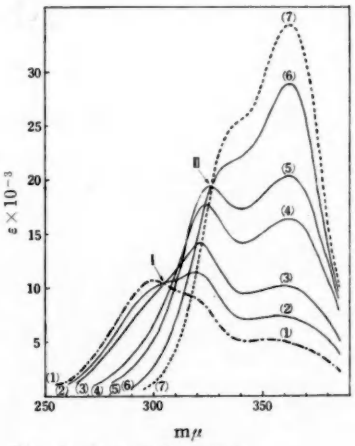


Fig. 5. Isosbestic points.
I: 305 mμ (ε=10400),
II: 327 mμ (ε=19300).
pH: (1) 0.2, (2) 0.3, (3) 0.5, (4) 1.0, (5) 1.3, (6) 2.0, (7) ca. 6.0.

Based on this consideration, one may account for the experimental facts as follows; the second dissociation occurs to produce the more stable croconate ion before the neutral acid molecule I is completely dissociated into the monoanion. When measuring pK_a values spectrophotometrically, the ultraviolet spectrum of each molecular species must be known[8,9]. For example, with the β-diketone compounds studied by B. Eistert et al.[8], the pK_{a1} and pK_{a2} were determined from the spectra of the three species, i.e., the enol oxonium cation, the neutral enol and the enol anion. In the case of croconic acid, the dissociations are not stepwise, and it is impossible to obtain the absorption curve of the monoanion. Furthermore, the curve of the undissociated acid can not be obtained under the conditions studied.

Thus the values of pK_{a1} and pK_{a2} in aqueous solution can not be measured, but it may be deduced that the first and the second dissociations both occur in the region below pH 2[10].

7) The following is worthy of notice; although the acid has the structure I both in strongly acidic aqueous solution and in acidic methanolic solution, the absorptions in these two solutions are different from each other (Fig. 3-(2), Fig. 4-(1)). One possible interpretation of this phenomenon is that in the acidic aqueous solution the lone pair electrons of the hydroxyl groups are able to conjugate with the annular π-electrons, whereas this is not the case in the acidic methanolic solution. However, the exact nature of the role played by solvents is not clear.

8) B. Eistert et al., *Chem. Ber.*, **87**, 108, 1513 (1954).

9) J. E. DeVries et al., *J. Am. Chem. Soc.*, **76**, 1008 (1954).

10) The pK_a can be obtained by plotting the absorbance against the pH at a suitable wave length (315 mμ). The curve obtained is distorted from the usual sigmoid shape on accout of the abnormal dissociations, and the estimation of the acidities is difficult. However, it is roughly estimated that the first dissociation occurs below pH 1 and the second one between pH 1~2.

Dipole moment.—The dipole moment of croconic acid is 9 to 10 D in dioxane. This large value is explicable only on the assumption that it has structure I. The dimethyl croconate has a dipole moment of 5.7~6.0 D and this is also illustrated on the basis of structure I. For further details, see following report on dipole moment measurements.

Infrared spectrum.—(i) The infrared spectra of croconic acid are shown in Fig. 6-(1) and -(2). A broad band is observed around 3000 cm^{-1}, which is located at a higher frequency (3500 cm^{-1}) in potassium bromide than in Nujol (2600 $cm.^{-1}$); this band disappears when the wet method of potassium bromide is applied. In the region of 1500~1800 $cm.^{-1}$, the bands taken in Nujol are somewhat different from those in potassium bromide, and their relative intensities are also different in both cases. The main bands are as follows: 1755, 1720 (w), 1655, 1630, 1540 (in Nujol); 1755, 1720, 1665, 1640, 1600, 1560 (shoulder), (in potassium bromide).

In the finger-print region, the spectra in potassium bromide and in Nujol have little resemblance. It is worth while to

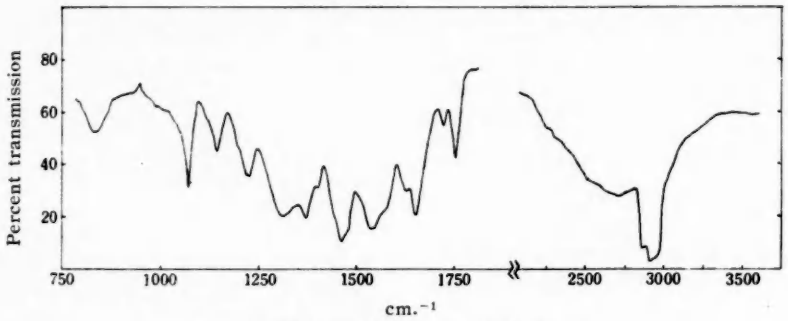


Fig. 6-(1). Croconic Acid (Nujol).

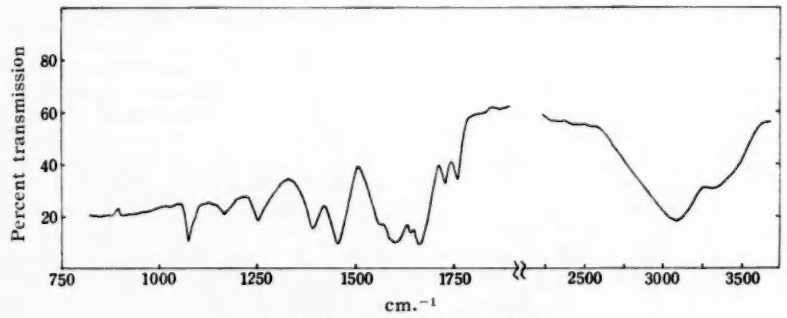


Fig. 6-(2). Croconic Acid (KBr).

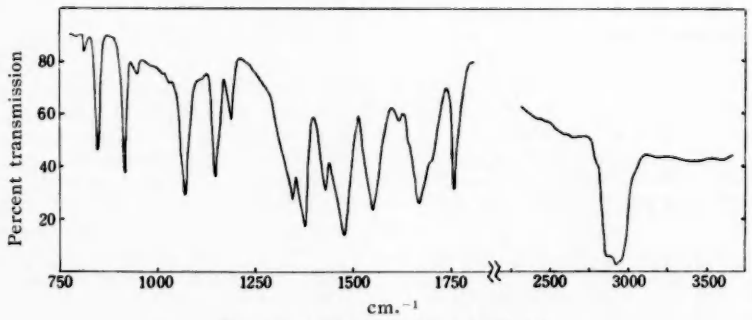


Fig. 7. Dimethyl croconate (Nujol).

notice the sharp band at 1075 cm^{-1}. This band is observed not only in the acid, but in the dimethyl derivative in Fig. 7.

(ii) As expected, there is no absorption band near 3000 cm^{-1} in the spectrum of the dimethyl derivative (Fig. 7). The main bands in the 1500~1800 cm^{-1} region are as follows: 1757, 1695 (shoulder), 1655, 1610, 1550. All the bands are sharp in comparison with those of the acid, and in the finger-print region, there is no band corresponding to the band of the acid except the band at 1075 cm^{-1} described before.

(iii) The spectra of the various metallic salts of the acid were measured (Fig. 8), in order to examine croconic acid in the ionic state. A strong broad band in the region of 1300~1700 cm^{-1} was common to all samples, and besides this, a few weak bands were observed. The bands in the finger-print region are small in number and weak.

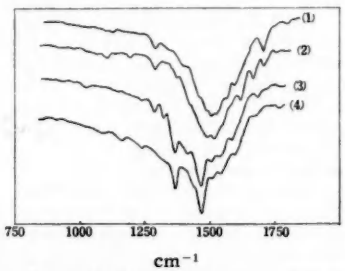
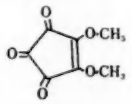


Fig. 8. Metallic salts of croconic acid.
(1) K (2) Ba (KBr)
(3) Ag (4) Cu (Nujol)

(iv) Some of the deductions from these spectra are as follows. Since the molecule is a compact system of conjugated groups in which intense coupling is expected to be present, the assignment of bands to specific groups is almost impossible. Nevertheless, assignments to a limited extent are possible. The band at 1755 cm^{-1} observed in both the acid and the dimethyl croconate is considered to originate from the $\rangle C{=}O$ groups. From the position of this band, the possibility is excluded that the acid might have the three-membered ketonic structure II. A four-membered ring ketone[11] absorbs at 1775 cm^{-1}, and if II is the actual case, the absorption would be expected to be even higher. Because of the broad bands of the acid, an exact comparison of the bands between the acid and the dimethyl croconate is difficult. However, approximate correspondences in their positions and intensities are observed, when the bands in the carbonyl region are compared.

The structure of the dimethyl croconate is believed to be VI, (see the section of ultraviolet spectrum and the report[6] on dipole moment measurement), and the similarity of the bands in the carbonyl region of the two compounds leads to the inference that the acid has structure I in its crystalline state.



(VI)

The broad band[12] near 3000 cm^{-1} is considered to be one due to a strong hydrogen bond. The band position of the hydrogen bond changes when the spectrum is taken in Nujol and in potassium bromide. The position of the hydrogen-bonded $\nu_{O\text{-}H}$ band suggests a stronger bond in the sample mulled in Nujol.

The metallic salts show besides the very strong and broad band near 1500 cm^{-1} only several weak absorptions. This experimental result is explained by consideration of a symmetric structure IV for the croconate ion. In this structure, all bonds exist in a state more or less intermediate between that of single and double bonds, and the strong broad band at 1500 cm^{-1} is presumably a summation of the absorptions arising from these intermediate $\rangle C{\cdots}O$ bonds. It is well known that the absorptions of simple compounds with highly symmetrical structures are simple, i. e., the tropylium ion[13], and this interpretation is probably applicable to the present case also.

11) Whiffen et al., *J. Chem. Soc.*, **1946**, 1005.

12) In carboxylic dimers, bands at $\simeq$1400 and $\simeq$1300 have been assigned to the coupling of in plane O-H bending and C-O stretching vibrations, and a band at $\simeq$940 to the out of plane O-H bending vibration (Sheppard and Hadži). Similar sets of bands are present in the spectra of dimedone and 2-hydroxy-1, 4-naphthoquinone, and accordingly it is presumed that somewhat analogous strong dimer rings are present in these two compounds. Croconic acid shows bands at 1455, 1245 and 800 cm^{-1} (in potassium bromide), and 1462, 1235 and 820 cm^{-1} (in Nujol), whereas these bands are absent in the spectrum of the dimethyl croconate (the band at 1430 cm^{-1} is probably due to $-CH_3$). It would be intriguing to assume the presence of a similar dimerization (intermolecular hydrogen bond) tentatively in the case of croconic acid.

13) W. v. E. Doering et al., *J. Am. Chem. Soc*, **76**, 3203 (1954).

Results

(A) State in solution.—In solution, croconic acid takes three different forms; the undissociated molecule I, the monoanion V and the dianion IV. The position of the equilibrium depends on the pH and the solvent used, as summarized roughly in Table I.

TABLE I
CROCONIC ACID IN SOLUTION

	Alkaline	Neutral	Acidic	Strong Acidic
Water	IV	IV	I, IV, V	I
Methanol	IV	IV	I, IV, V	I
Ethanol	IV	I, IV, V	I, IV, V	I

The undissociated molecule, the structure of which turned out to be I on the basis of the ultraviolet spectrum of dimethyl croconate VI exists only in strongly acidic solution. There seem to be two types of ultraviolet spectra corresponding to the undissociated molecule and this seems to suggest some effect of the lone pair belonging to the oxygen atoms of hydroxyl groups (Figs. 3-(2) and 4-(1)). Little is known about the monoanion V, existence of which is noticed from the ultraviolet spectrum. Finally, the croconate ion IV is a stable and highly symmetrical dianion, and absorbs strongly at a higher wave length than the undissociated molecule in the ultraviolet spectrum[14]. A similar bathochromic shift in the symmetric ion is observed in the β-diketone system. Namely, the absorption of the highly symmetrical enolate ion occurs at a wave length higher than that of less symmetrical enol[8]. The great stability of the croconate ion accounts for the strong acidity of the two hydroxyl groups.

It is presumed that the keto-form III, if it exists at all, is contained only to a negligible extent.

(B) Solid state.—The dipole moment and the ultraviolet spectrum of the dimethyl croconate support structure VI for this compound. Moreover, structure I for the free acid becomes favorable from the similarity of infrared spectra of the acid and the dimethyl croconate. The characteristic feature of the infrared spectrum of the acid is the strong hydrogen-bonded band and a set of bands similar to those observed with dimeric carboxylic acids, which disappear upon methylation. The three-membered ketonic structure II is excluded from the C=O band at 1755 cm^{-1}. The croconate ion is formed in the metallic salt, and only a few bands are observed because of the symmetrical structure of this ion.

Experimental

The ultraviolet spectra were measured with a Hitachi Spectrophotometer. Infrared spectra were measured with a Hilger H 800 Model, equipped with rock-salt prisms.

Croconic acid.—Glyoxal was used as the starting material, and the sample was recrystallized twice (for details of synthesis, see the following paper[15]).

Ultraviolet spectra of croconic acid.—Table II shows the positions and intensities of the absorptions of croconic acid and its dimethyl derivative. The dimethyl croconate, easily hydrolyzed even in the air, was weighed as rapidly as qossible and dissolved in methanol; once in solution, it is stable. When the solution was placed under the sun light, the intensity of the whole absorption was somewhat weakened, but the extent was not as considerable as in the case of croconic acid (croconic acid is decomposed rapidly by the sun light). The solvent methanol used for the dimethyl croconate was free from water (using metallic calcium) and distilled.

TABLE II

Solvent	Neutral		Alkaline		Acidic		Strong acidic	
	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
	(mμ)			(Croconic acid)				
Water	365	4.6	365	4.6	323 363	4.3 4.2	300	4.2
Ethanol	365	4.6	363	4.6	—	—	296	4.16
Methanol	298 360	4.2 3.9	—	—	—	—	—	—
Dioxane	295	4.16	—	—	—	—	—	—
				(Dimethyl croconate)				
Methanol	292	4.1	—	—	—	—	—	—

14) The calculation[6] based on the molecular orbital method agrees with this experimental fact.
15) K. Yamada et al., This Bulletin, **31**, 550 (1958).
16) B. O. Heston et al., *J. Am. Chem. Soc.*, **56**, 1462 (1954).

Two absorption peaks are clearly present in the weakly acidic aqueous solution and the ethanol solution of the croconic acid. These absorption curves differ from that of the croconate ion measured in water or in methanol. Croconic acid is presumed to exist as an equilibrium mixture among the neutral molecule and the ions (mono- or di-ion). The "solvent basicity" increases in the sequence of ethanol, methanol, and water[16], and thus the equilibrium is shifted towards the ions to a greater extent in the same order. The curves in Figs. 1-(3) and 2 are a composite of the three species.

Isosbestic point of croconic acid.—A stock solution containing 3.638 mg. of croconic acid in 50 ml. of water was prepared. Various solutions having different pH (about 0.1~2.5) were prepared as follows. One normal solution of hydrochloric acid was diluted suitably to make a solution having the desired pH. The ionic strength of every solution was adjusted to that of 1 N hydrochloric acid by adding the proper quantity of 1 M sodium chloride solution. The stock solution (1 ml.) was exactly added to 9 ml. of the solution prepared as noted above. The curve 7 in Fig. 5 was measured in 1 M sodium chloride solution. The absorption curve at pH 2.4, though not shown in Fig. 5, almost coincides with that in the neutral solution. As described previously in this paper, the isosbestic point at 305 mμ (ε=10400) is incomplete and the curves at pH 0.2, 0.3, 0.5, do not intersect at one point strictly. The absorption curves taken in the pH range of 0.6~1.2 pass neither of the isosbestic points. There thus exists an eqilibrium of three components in this pH region.

Metallic salts of croconic acids.—Various metallic salts were obtained easily from croconic acid. Potassium salt and barium salt were obtained during the synthetic process, or adding potassium hydroxide or barium hydroxide (or chloride) to the aqueous solution of croconic acid. The potassium salt loses the crystal water (2 moles) in a desiccator (yellow crystal), but this is easily absorbed again when placed in the air (orange crystal). Cupric salt, lead salt, etc., were obtained from the chloride or nitrate of the metal and the aqueous solution of croconic acid. The silver salt was prepared from silver nitrate. On account of the strong reducing property of croconic acid, the silver nitrate was partly reduced, and metallic silver was deposited. The silver salt was filtered at once under protection from the sun light.

Summary

The structure of croconic acid in solution and in the solid state has been studied. The undissociated molecule is represented by structure I and the ion by structure IV.

The authors are greatly indebted to Assistant Professor K. Nakanishi and Mr. T. Goto for the many helpful discussions we have had during the course of this work. The authors also express their gratitude to Professor M. Kubo for his guidance and interest in this research, and to Mr. O. Shimomura and Mr. M. Miyazaki for their excellent technical assistance. Our thanks are also due to the Ministry of Education for financial support of this research.

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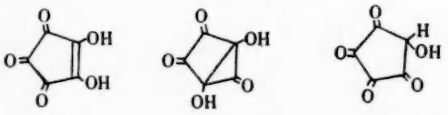
Ring Enlargement of Croconic Acid

By Kiyoyuki YAMADA and Yoshimasa HIRATA

(Received March 3, 1958)

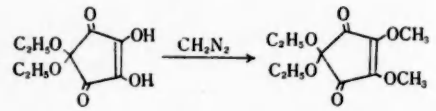
The structures I[1], II[2] and III[3] (III, as a tautomer of I in an aqueous solution) have been so far presented for croconic acid.



(I) (II) (III)

With the intention of clarifying the structure, various properties of the acid itself and its derivatives have been studied, and it has been concluded that the acid has the structure I and that a strong hydrogen bond is present[4].

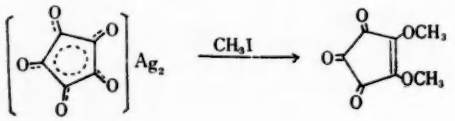
In 1938, R. Malachowski prepared various derivatives of croconic acid, and examination of its structure by chemical methods finally led to the formula I. In his research, treatment of the diethyl acetal of croconic acid with diazomethane yielded its dimethyl derivative (liquid).



On the other hand, during the course of our studies, it was noticed that the reaction between the acid and ethereal diazomethane yielded orange needles. On the basis of its properties and analyses, this reaction product appeared to be trimethoxy-*p*-benzoquinone resulting from ring enlargement of the acid and successive methylation. Accordingly, this quinone was synthesized from pyrogallol through a route which left no doubt as to the correctness of the structure of the synthetic product[5]. Comparison of infrared and ultraviolet spectra and a mixed melting point test showed the two specimens to be identical. Since croconic acid is insoluble in ether, the reaction is heterogeneous. The quinone is presumably formed by the following mechanism.

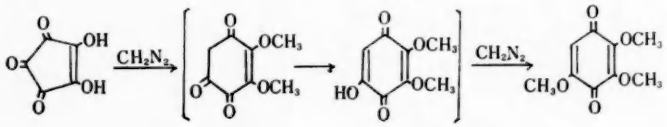
Though there are many cases in which the normal product is also produced in anomalous diazomethane reactions, careful scrutiny of the product showed that no dimethyl derivative of croconic acid had been formed. It is interesting that the abnormal reaction takes place in case of croconic acid itself, but does not in case of the acetal derivative.

For the purpose of comparison, the dimethyl ether of the acid was prepared by treating the silver salt with methyl iodide in absolute ether. The compound is, of course, different from the product obtained in the case of the reaction described above. It was, as expected from its structure, easily hydrolyzed to croconic acid even by the moisture in the air.



Experimental

Croconic acid.—Croconic acid is usually prepared by oxidation of an alkaline (potassium carbonate) solution of diaminotetrahydroxybenzene with manganese dioxide, or by treatment



1) R. Malachowski, *Ber.*, **71**, 2206 (1938).
2) R. Nietzki et al., ibid. **18**, 510, 1833 (1885), **19**, 294, 301, 772 (1886), **20**, 1617, 2118 (1887); G. E. Carpéni, *Compt. rend.*, **203**, 601 (1938).
3) Y. Hirata et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **69**, 63 (1948).
4) K. Yamada et al., This Bulletin. **31**, 532 (1958).
5) H. O. Huisman, *Rec. trav. chim.*, **69**, 1145 (1950).

of sodium rhodizonate with an excess of alkali (R. Nietzki)[6]. With the former route the preparation of the diaminotetrahydroxybenzene is troublesome; with the latter route the yield is poor. In the present studies, sodium rhodizonate, easily obtainable from glyoxal[7], was oxidized with manganese dioxide to give potassium croconate in fairly good yield. Namely, to a solution of 7 g. of sodium rhodizonate in 350 ml. of water were added 30 g. of potassium carbonate and 20 g. of manganese dioxide which was freshly prepared from potassium permanganate. After the suspension was refluxed with shaking for one hour, it was filtered at once, and the potassium croconate appeared in the filtrate after cooling. The filtrate containing crystalline potassium croconate was acidified with hydrochloric acid, when the crystals disappeared. The addition of the barium chloride solution to this acidic solution gave 7.6 g. (ca. 85%) of golden barium croconate.

An excessive amount of barium croconate was added to a solution of sulfuric acid (3 N), and the mixture was warmed for about one hour. Excess barium croconate was filtered and the yellow filtrate was concentrated at 40° under reduced pressure, to give crude croconic acid.

The purification was carried out as follows. A saturated solution of crude croconic acid in warm water or alcohol (50°~60°) was cooled in an ice box, upon which there was obtained a small amount of crystals. The remaining solution was concentrated in a desiccator, when the second crop of crystals were obtained in the form of needles or plates. Croconic acid has no melting point, but becomes brown near 150°, and gradually decomposes.

Anal. Found: C, 42.16; H, 1.80. Calcd. for $C_5H_2O_5$: C, 42.25; H, 1.41%.

Reaction product of croconic acid with diazomethane.—A dry ethereal solution (15 ml.) of diazomethane prepared from nitrosomethylurea (containing CH_2N_2 0.007~0.009 M) was placed in a small flask with cooling, and to this 100 mg. (0.0007 M) of croconic acid was added. At first, the reaction occurred on the surface of the acid and the acid gradually dissolved. After thirty minutes, the reaction ceased. The solution became orange, and was left for a while. The orange crystals appearing on the surface of the flask were filtered. The filtrate was concentrated but this only gave an oily residue. The orange crystals were recrystallized from methanol, m. p. 157~158° (quinone prepared from pyrogallol, m.p. 158~160°), yield, 40 mg. Ultraviolet absorption maximum $\lambda_{max.}$ 288 mμ ($\log \varepsilon$ 4.08 in ethanol).

Anal. Found: C, 54.59; H, 5.49. O-CH_3 (Zeisel): 45.9% (1.96 groups). Calcd. for $C_9H_{10}O_5$: C, 54.55; H, 5.09%.

Purification of the oily material was undertaken, in order to examine the existence of another product, but nothing could be detected except that a further small amount of the above quinone was obtained. When a methanolic solution of croconic acid was added to the ethereal diazomethane, the yield was poor and the amount of the oily product increased.

Dimethyl croconate[1].—It was necessary that all the solvent and the reagents should be quite free from water and that the flask provided with a calcium chloride tube should be used. Since the reaction was heterogeneous, it was necessary to stir occasionally. The reaction was complete after one day at room temperature (10~15°). The product was recrystallized from benzene. Orange prism, m. p. 113~114°.

Anal. Found: C, 48.96; H, 3.65. Calcd. for $C_7H_6O_5$: C, 49.42; H, 3.56%.

The analytical data do not quite agree with the calculated values, probably owing to the hydrolysis of the sample in the air. When placed in dilute hydrochloric acid, the dimethyl croconate was at first insoluble, but after several seconds it started to dissolve fairly rapidly. The aqueous solution was warmed for thirty minutes, and upon evaporation of the solvent there was obtained free croconic acid. The free croconic acid itself is very soluble in water.

Summary

The reaction of croconic acid with diazomethane gives instead of its simple methylated product, a compound with an enlarged ring. Trimethoxy-*p*-benzoquinone was synthesized from pyrogallol, and was identified with the compound obtained from croconic acid.

The authors wish to make grateful acknowledgements to Mr. S. Senoh, Osaka City University, for microanalyses. They also express their gratitude to the Ministry of Education for financial support of this research.

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6) R. Nietzki et al., *Ber.*, **18**, 1842 (1885), **19**, 293 (1886).
7) B. Homolka, *Ber.*, **54**, 1393 (1921).

The Dipole Moments and Molecular Structures of Croconic Acid and Dimethyl Croconate

By Masamitsu WASHINO, Kiyoyuki YAMADA and Yukio KURITA

(Received March 3, 1958)

One of the present authors (K. Y.) and his co-workers have carried out extensive studies on the chemical properties of croconic acid and determined its structure to be cyclopentene-1-diol-1,2-trione-3,4,5[1]. They have measured the dipole moments of croconic acid and dimethyl croconate. Comparing the observed moments with those calculated by the method of molecular orbitals, they have undertaken to determine the electronic structures of these molecules as well as the geometrical arrangements of hydroxyl and methoxyl groups.

Experimental

Croconic acid and dimethyl croconate were synthesized and purified by one of them (K. Y.)[1]. Since these compounds were hygroscopic and the latter compound was readily hydrolyzed and gave the former, solvents were dried carefully. The dielectric constants and densities were measured of the solutions in dioxane or benzene. Because of the small solubilities, the measurements could not be extended to solutions of concentrations above 0.1 weight per cent. Therefore, it was difficult to determine the dipole moment very accurately.

The apparatus and the method of measurements were the same as used in our earlier works[2] except that a silvered cell of Sayce-Briscoe type[3] was used for the benzene solutions of dimethyl croconate. The Halverstadt-Kumler's method was employed. The dependence of the dielectric constants of the solutions of croconic acid in dioxane upon concentration was abnormal, the value of $\Delta\varepsilon/w$ increasing sharply with the decrease in concentrations. This fact suggests association or dissociation taking place. The results are shown in Tables I and II, where the same notations are used as in the previous reports[2].

TABLE I
DIELECTRIC CONSTANT AND DENSITY INCREMENTS OF SOLUTIONS OF CROCONIC ACID AND DIMETHYL CROCONATE

	Temp.	$w\times10^6$	$\Delta\varepsilon\times10^4$	$\Delta d\times10^5$
Croconic acid	25°C	80	68	—
in dioxane		233	156	—
		527	273	28
		1233	454	101
	35°C	140	91	0
		269	151	0
		507	220	0.3
		761	254	1.3
		937	264	2.8
Dimethyl croconate	30°C	306	53	—
in benzene		448	92	1.7
		645	134	—
		926	182	3.5
		1271	273	5.1

Discussion

The dipole moments of croconic acid and dimethyl croconate are high*. This indicates an appreciable contribution of polar structures to the ground state. The difference between the moments of the two compounds is as large as about 3~4 D. Since the group moment of C—OH is nearly the same as that of C—OCH_3 in its magnitude and also in its direction, the moments of the two compounds should be of the same order, unless an appreciable difference exists between the electronic and/or geometrical structures of the two compounds.

In calculating the moments of these compounds, one must take into account rotations about C—O single bonds. The moments were calculated for four conceivable configurations shown in Fig. 1. In the case of planar configurations, A and B, in which two OH or two OCH_3 groups lie in the ring plane, the two lone pairs belonging to the oxygen atoms conjugate with the rest of the molecule, so that twelve π-electrons are distributed

1) K. Yamada, N. Mizuno and Y. Hirata, This Bulletin, **31**, 543 (1958).

* Accordingly, the structures having small moments, such as II or III in our previous report,[1] are not conceivable.

2) Y. Kurita, T. Nozoe and M. Kubo, ibid., **26**, 242 (1953).

3) M. Kobayashi, Y. Kurita and M. Kubo, *Chemistry and Chemical Industry* (*Kagaku to Kogyo*), **10**, 138 (1957).

TABLE II

MOLECULAR POLARIZATION AND DIPOLE MOMENTS

Compounds	Solvent	Temp.	ε_1	d_1 (g./cc.)	α	β (g./cc.)	$P_{2\infty}$ (cc.)	P_{A+E} (cc.)	μ(D)
Croconic acid	dioxane	25°C	2.2084	1.02755	80	0.86	1880	31	9.5 ±0.5
		35°C	2.1888	1.01565	76	0.00	1817	31	9.3 ±0.3
Dimethyl croconate	benzene	30°C	2.2625	0.86695	21	0.39	726	35	5.85±0.15

TABLE III

MOLECULAR ORBITAL ENERGIES AND WAVE FUNCTIONS[b]

Planar configuration

Symmetry[c]	ω[a]	c_1	c_2	c_3	c_4	c_5	c_6
S	−3.8480	0.0929	0.1213	0.1677	0.1283	0.3426	0.5713
A	−3.4960	0	0	0.1060	0.1003	0.2290	0.6529
S	−3.1358	0.5255	0.4220	0.2901	0.3612	−0.0231	−0.2400
A	−2.7504	0	0	0.3230	0.6088	0.0275	−0.1556
S	−2.5196	0.6784	0.2493	−0.1656	−0.4507	−0.0292	0.0858
S	−0.7605	0.2686	−0.2355	−0.2795	0.3189	−0.4280	0.2703
S	0.1648	0.3738	−0.5723	−0.2172	0.1419	0.4074	−0.1819
A	0.2037	0	0	0.4995	−0.3206	0.3516	−0.1553
A	2.0427	0	0	0.3673	−0.1285	−0.5685	0.1595
S	2.0989	0.2076	−0.6017	0.4847	−0.1672	−0.1791	0.0498

Perpendicular configuration

S	−3.2515	0.4750	0.4204	0.3476	0.3927	0.1543	
A	−2.7913	0	0	0.3425	0.6120	0.0903	
S	−2.5447	0.7222	0.2782	−0.1568	−0.4070	−0.1015	
S	−1.2804	0.1606	−0.0817	−0.1659	0.3260	−0.5916	
S	0	0.4264	−0.6030	−0.3015	0.2132	0.3015	
A	0	0	0	0.4472	−0.3162	0.4472	
A	1.7913	0	0	0.4275	−0.1595	−0.5402	
S	2.0766	0.2126	−0.6129	0.4860	−0.1686	−0.1580	

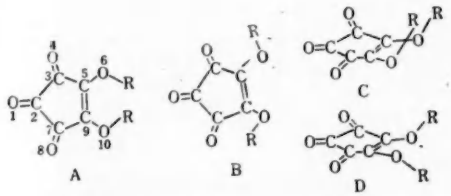
a) $\omega=(\alpha-E)/\beta$.

b) E: the energy of molecular orbital $\phi=\sum_r c_r\chi_r$. χ_r: atomic orbital of an r-th atom. As to numbering of atoms, see Fig. 1. Parameters used are as follows: Coulomb integrals are α, $\alpha+2\beta$, and $\alpha+3\beta$ for carbon atoms, carbonyl oxygen atoms and oxygen atoms of OH and OCH_3, respectively. Resonance integrals are β and $\sqrt{2}\beta$ for C-C and C-O bonds, respectively.

c) The suffixes S and A denote the symmetry properties of the molecular orbitals. For symmetric molecular orbitals, $c_7=c_3$, $c_8=c_4$, $c_9=c_5$ and $c_{10}=c_6$. For antisymmetric molecular orbitals, $c_7=-c_3$, $c_8=-c_4$, $c_9=-c_5$ and $c_{10}=-c_6$.

among ten atoms. On the other hand, for the perpendicular configurations, C and D, in which two OH or two OCH_3 groups lie in the plane perpendicular to the ring, the conjugation decreases to its minimum. Then, it can be treated as a system of eight π-electrons distributed among eight atoms.

It is difficult to calculate adequately the moment of a molecule conjugated to such an extent as in croconic acid or dimethyl croconate from the vector addition of relevant bond moments. It is generally accepted that the simple method of molecular orbitals, which neglects mutual re-



Planar configuration — Perpendicular configuration

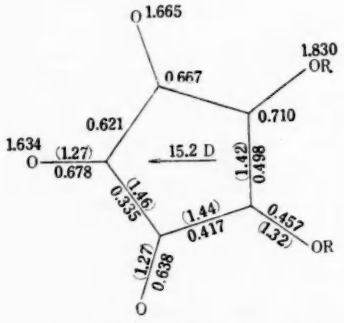
Fig. 1. Croconic acid (R=H) and dimethyl croconate ($R=CH_3$).

pulsion between electrons, always gives too high values for the theoretical moments. Orgel and his co-workers[4] presented an equation to calculate a total moment with due regard to mutual repulsion between electrons.

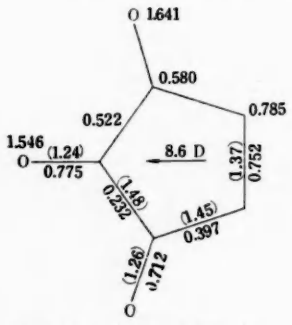
$$\vec{\mu}_T = \vec{\mu}_\sigma + \vec{\mu}_\pi / 1.6 \qquad (1)$$

They applied this equation to eighteen conjugate heterocyclic compounds and obtained theoretical moments in agreement with the observed ones within 0.30 D in magnitudes and 10° in directions. Following their procedure, we calculated the dipole moments.

In Table III are shown the energies and the coefficients of atomic orbitals in molecular orbitals constructed from π-orbitals belonging to atoms participating in conjugation. Ten and eight atoms are involved in the planar and perpendicular configurations, respectively. In Fig. 2 are shown the corresponding molecular diagrams accommodated with twelve or eight



Planar configuration



Perpendicular configuration

Fig. 2. Molecular diagrams: π-electron densities, bond orders, bond lengths (in parentheses), and μ_π.

4) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

π-electrons allotted to the molecular orbitals of low energies. The bond lengths were calculated from bond orders using the relation described in a preceding report[5]. In each diagram, the estimated μ_π is shown, which was obtained by assuming that the pentagon ring is approximately regular, that the carbon-oxygen bonds lie along the lines from the center of the ring to the respective carbon atoms, and that the bond distances are as given above. On the other hand, μ_σ was calculated with the assumption that the bond moments of OH and OCH_3 were equal to 1.5 D and 1.2 D, respectively, and that the valency angles $\angle COH$ and $\angle COCH_3$ were 105° and 110°, respectively. The total moments calculated from equation 1 are shown in Table IV, together with the observed moments.

TABLE IV
DIPOLE MOMENTS (D)

Configuration		Croconic acid	Dimethyl croconate
Planar	A	8.4	8.8
	B	10.4	10.3
Perpendicular	C	6.7	6.5
	D	6.0	6.0
Observed		9~10	5.7~6.0

The moment of dimethyl croconate can adequately be explained by the perpendicular configurations. The planar configurations are unlikely in view of the steric hindrance acting between the methyl groups or between the methyl group and the carbonyl oxygen atom. The observed moment of croconic acid is in good agreement with those of the planar configurations. In these configurations, the conjugation within the molecule can attain its maximum possible extent. Moreover, a hydrogen bond can be formed between the OH group and carbonyl oxygen or between the OH groups. The hydrogen bond formation stabilizes the molecule and increases the trend of electron attraction of carbonyl oxygen.

The first excitation energy associated with π-electron was calculated as 0.925β, 1.280β and 0.813β* for the planar and perpendicular configurations and for a croconate ion $C_5O_5^{--}$, respectively. This energy level can be shown to be capable of accounting for the spectral features of

5) Y. Kurita and M. Kubo, This Bulletin, **24**, 13 (1951).

* It was calculated with the assumption that croconate ion is planar and symmetrical and the Coulomb integral of oxygen atom is $\alpha + 2.4\beta$.

the acid and its dimethyl ester as well as the changes in their spectra with solvents[1].

Summary

The dipole moments of croconic acid and dimethyl croconate were measured in dioxane and benzene solutions, respectively, as 9~10 D and 5.7~6.0 D. The moments of these molecules were calculated theoretically for several conceivable configurations by the method of molecular orbitals. The results confirm the structure presumed from evidences in organic syntheses. The accumulation of π-electrons on carbonyl oxygen is chiefly responsible for the large dipole moments, the effect being stronger in the acid. The hydroxyl groups of croconic acid lie in the ring plane, whereas the methoxyl groups are out of the ring plane to minimize the steric hindrance.

The authors wish to express their cordial thanks to Professors M. Kubo and Y. Hirata for their guidance and encouragement. Their thanks are also due to the Ministry of Education for financial support of this research.

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*Formation and Aging of Precipitates. VII. Habit of Crystals in Vanadium Pentoxide Sols by Electron Microdiffraction Method**

By Kazuyoshi TAKIYAMA

(Received November 21, 1957)

Morphological studies on the crystals in three kinds of vanadium pentoxide sol, such as Biltz-, Müller-, and ion-exchange sols, were reported in a previous paper[1]. Watson, Heller and Wojtowicz[2] indicated the electron diffraction patterns of the crystals in Biltz sol and showed that the patterns verified the crystal growth. This paper describes the identification of crystals in three kinds of sol and the crystal habit of the Biltz sol crystals.

Experiments and Results

Identification of Crystals in Various Sols by Electron Diffraction Method.— Electron diffraction patterns obtained from the crystals in Biltz-, Müller- and ion-exchange sols, reported in the previous paper[1], are shown in Fig. 1. From these patterns the interplanar spacings of each crystal were calculated and the diagrams

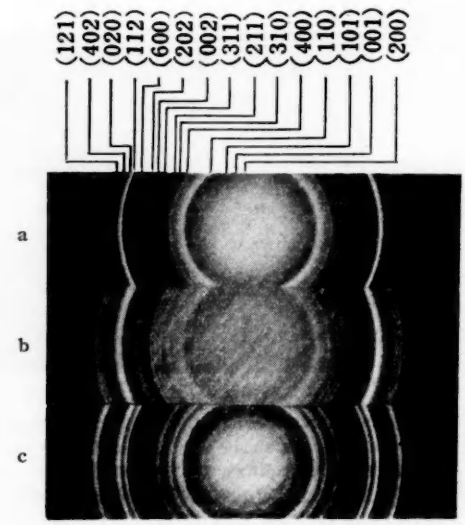

Fig. 1. Electron diffraction patterns of crystals in various sols.
a. Biltz sol
b. Müller sol
c. Ion-exchange sol

* Some parts of this experiment were published in *Proc. Japan Acad.*, **30**, 752 (1954) and were read in advance at the First Regional Conference on Electron Microscopy in Asia and Oceania on October 27, 1956.

1) K. Takiyama, This Bulletin, **31**, 329 (1958).

2) J. H. L. Watson, W. Heller and W. Wojtowicz, *Science*, **109**, 274 (1949).

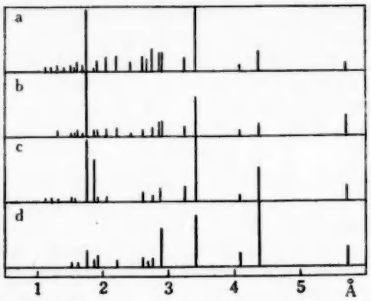

Fig. 2. Diagrams of electron diffraction patterns obtained from crystals in various sols.
a. Biltz sol
b. Müller sol
c. Ion-exchange sol
d. Vanadium pentoxide crystal by means of X-ray diffraction method

of the patterns are shown in Fig. 2. The interplanar spacings of the crystals in every sol agree with those of vanadium pentoxide crystal determined by X-ray diffraction method[3], so that all of the crystals in the sols were identified with vanadium pentoxide.

The Habit of Crystals in Biltz Sol.— The crystals in Biltz sol grew like long fibers upon aging as described in the previous paper[1]. When an aged sol was mounted onto a specimen holder for electron microscopy by the usual method, the photograph was obtained which showed the network of fiber-like crystals as shown in Fig. 3a in the previous paper[1] and its electron diffraction pattern obtained by means of the selected area electron diffraction technique (electron microdiffraction method) was that of Debye-Scherrer rings as shown in Fig. 3a, in which interplanar spacings agreed with those of vanadium pentoxide. The tiny film formed on the surface of the aged sol contained tactoid as shown in Fig. 3b in the previous paper[1], in which the fibrous crystals were oriented parallel to one another. As the direction of the specimen, accordingly that of the fiber axis, was perpendicular to the electron beam, the electron diffraction pattern obtained from the tactoid was a typical fiber pattern as shown in Fig. 3b. Space indices of each reflection point are indicated in Fig. 4. As indicated in Fig. 4, the layer lines are $k=0, \pm1, \pm2, \cdots\cdots$, and the reflection points of (020) and (040) appear on the meridian. By measuring the distance of each layer line from the equatorial line, the fiber period can be calculated by the following equation

$$c = nL\lambda/r_n,$$

where c is the fiber period, L camera

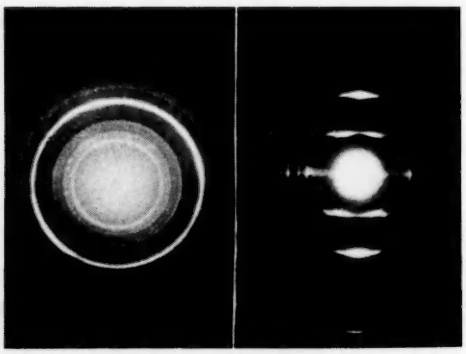

Fig. 3. Electron diffraction patterns obtained from the two types of crystals in one year old Biltz sol by the selected area electron diffraction technique.
a. Electron diffraction pattern obtained from the part of the network structure.
b. Electron diffraction pattern obtained from the part of the tactoid.

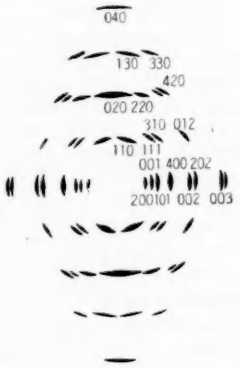

Fig. 4. Space indices of fiber pattern shown in Fig. 3b.

3) J. D. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 510 (1938).

length, λ wave length of the electron beam and r_n distance of the n-th layer line from the equatorial line. The value of $L\lambda$ was calculated from the Debye-Scherrer ring pattern obtained from an evaporated aluminum film used as a standard. The fiber period was calculated from 17 electron diffraction patterns as 3.56±0.011 Å which was in accord with the lattice constant of b-axis of vanadium pentoxide, that is b_0= 3.564Å[4]. So the fiber axis, the direction of the crystal growth, was also clearly confirmed as b-axis.

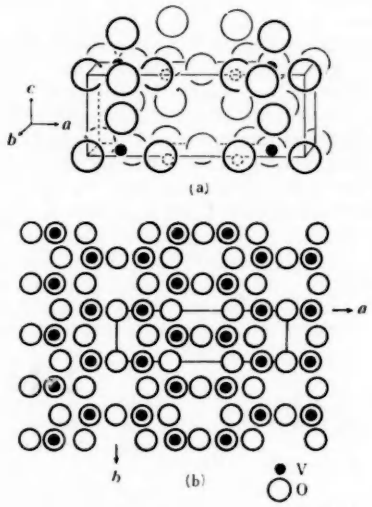

Fig. 5. a: Configuration of vanadium pentoxide crystal.
b: Projection of the structure of vanadium pentoxide crystal on (001).

The fibrous crystals in Biltz sol grew along the b-axis and no growth along the a- and c-axis occurred. The configuration of vanadium pentoxide crystal[4] and the structure projection on (001) of it are given in Fig. 5 a and b. The distribution of vanadium and oxygen atoms along the b-axis is denser than that along other axes. The direction of the growth of the fibrous crystals in Biltz sol agrees with the direction of the dense distribution of atoms.

Summary

The crystals in Biltz-, Müller-, and ion-exchange sols were all identified with vanadium pentoxide by the electron diffraction method.

The crystals in aged Biltz sol were fiber-like. The specimen prepared ordinarily gave rise to the Debye-Scherrer pattern and that of the tactoid corresponded to the fiber pattern. The fiber axis of the fibrous crystal was decided to be the b-axis.

The author wishes to express his sincere thanks to Professor Eiji Suito of Kyoto University for his guidance and discussion. The author particularly wishes to express his deep gratitude to Professor Masayoshi Ishibashi of Kyoto University for his discussion and encouragement during this work and is also indebted to Dr. Ryoichi Kiriyama of Osaka University for his advice.

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4) A. J. C. Wilson, "Structure Report", International Union of Crystallography, N.V.A. Oosthoek's Uitgevers, MIJ, Utrecht (1950), p. 232.

Molecular Rotations of Glucides in Relation to their Structures. V. The Internal Conformation of C^6—O Bond in D-Galactopyranose in the Aqueous Solution and the Direction of the Optical Axis of Methylol Group

By Shukichi YAMANA

(Received December 26, 1957)

On the basis of Kirkwood's polarizability theory, the author explained the physical meaning of the empirical rule which had been found by Hudson about isorotation among anomers of aldoses[1]. In this explanation, the author used a simple molecular model of hypothetically ideal shape for simplification of calculation and also assumed that the orientation of OH group of $(CH_2OH)^{5\beta}$ as regards the aldopyranose-ring is definite and similar in D-galactopyranose, D-glucopyranose and D-mannopyranose*1. But strictly speaking, the orientation of OH group in $(CH_2OH)^{5\beta}$ is affected by the neighboring atoms and accordingly it may not always be equal in the molecule of D-galactopyranose and D-glucopyranose in aqueous solution[4]. On the other hand, Kirkwood expected that C*-atom with which C_2H_5 group combines in *sec*-butyl alcohol would have a marked effect on the optical axis of C_2H_5 and consequently this axis would be supposed to be placed on the plane of C*-atom and C—C bond in C_2H_5 group, and this axis would be inclined to this C—C bond at the angle between 0° and 54°44′ (one half the tetrahedral angle)[6]. By this conception, the optical axis of $(CH_2OH)^{5\beta}$ in an aldopyranose-molecule is expected to be on the plane of C^5-atom and C^6—O bond and this axis would incline to the C^6—O bond at an angle of θ*2. (Fig. 1)

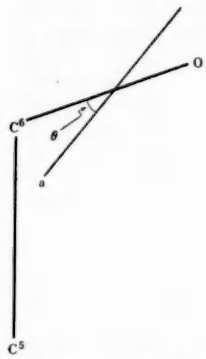

Fig. 1. Direction of the optical axis of $(CH_2OH)^{5\beta}$
a……optical axis.

According to this presumption, the author tried in this article, to calculate the values of the anomeric differences*3 in molecular models of aldopyranoses*4.

Molecular Model and Data Used

In the present calculation, Mc Donald

1) S. Yamana, This Bulletin, **30**, 207 (1957).

*1 By this treatment, $[\mu]^{20}_{D\,\text{calcd}}$, caused by the dynamical coupling effect of $(CH_2OH)^{5\beta}$ disappeared. Moreover, in order to simplify the calculations, the author assumed also in the previous papers[1-4] that, indifferently to its orientation, OH group has an optical axis of cylindrical symmetry directed along its bond to C atom with which it combines at resting state. In this case, OH group is treated as a single particle, like so-called pseudo-atom (ref. 5) of atomic weight, 17.008, indifferently to the position of H atom in this group. This state of OH group was called "isotropic" in the previous papers (1)(2). But, it never means that OH group is "optically isotropic".

2) S. Yamana, ibid., **30**, 203 (1957).

3) S. Yamana, ibid., **30**, 916 (1957).

4) S. Yamana, ibid., **30**, 920 (1957).

5) C. A. Coulson, *Quart. Rev.*, **1**, 144 (1947).

6) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

*2 The value of this angle θ may be expected to lie between 0° and 54°44′ (one half the tetrahedral angle).

*3 Ref. *2 in the previous paper 1. The anomeric difference is abbreviated to An. Diff., hereafter.

*4 Then, it became possible to presume the internal conformation of C^6-O bond in D-galactopyranose in aqueous solution and the angle of inclination of the optical axis, θ, of $(CH_2OH)^{5\beta}$.

TABLE I

Name	Unit Groups	$[M]_D^{20}$(W)	Ref.*10
α-D-glucose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.ma}$*10, Ring]	202.1°	a)
β-D-glucose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.ma}$, Ring]	33.7°	a)
α-D-mannose	[$(OH)^{1\alpha}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.ma}$, Ring]	52.8°	a)
β-D-mannose	[$(OH)^{1\beta}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_2OH)^{5\beta.ma}$, Ring]	−30.6°	a)
α-D-galactose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.ga}$*11, Ring]	271.5°	a)
β-D-galactose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.ga}$, Ring]	95.1°	a)
β-L-arabinose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	286.1°	a)
α-L-arabinose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	115.6°*12	a)

and Beevers' molecular model*5 was used. Unit groups in the molecules of several aldopyranoses and corresponding values of molecular rotations are shown in Table I*7,*8.

Except the position of their optical centers, the optical data for OH group and H atom in the previous paper 2, are used again without any correction. Values of mean polarizability α and of anisotropy ratio β of CH_2OH group are 2.87×10^{-24} (cc)[c] and 0.35[d] respectively. It is supposed that CH_2OH group has its optical axis of cylindrical symmetry which is placed on the plane of C^5-atom and its C^6—O bond, and this axis inclines to the C^6—O bond at an angle θ*2 (cf. Fig. 1). It is also supposed that the optical center of OH group which combines with C atom is located at the center of mass of C—(OH) bond, and the optical center of $(CH_2OH)^{5\beta}$ is at C^6-atom*13. The refractive indices

*5 Ref. *4 in the previous paper 4. This model seems to show the molecule-shape of an aldopyranose in aqueous solution more accurately than the ideal model*6 does.

*6 Ref. "Molecular Model and Data Used." in the previous papers 4 and 1.

*7 Isbell and Pigman observed $[M]_D^{20}$(W) of aldopyranoses in details when studying the mutarotation-curves. In this paper, Isbell and Pigman's data were used. By using their data, it became apparent that An. Diff. of D-galactopyranose is not exactly but approximately equal to that of D-glucopyranose.

*8 As it has not been confirmed that D-talopyranose has C 1 conformation in its aqueous solution, this sugar is not treated in this paper. If D-talopyranose has C 1 conformation, the following data would be used for α- and β-isomers.

Name	Unit Groups	$[M]_D^{20}$(W)	Ref.
α-D-talose	[$(OH)^{1\alpha}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.ga}$*9, Ring]	122.5°	a)*10
β-D-talose	[$(OH)^{1\beta}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta.ga}$, Ring]	23.8°	a)

*9 Ref. *11 in this article. When the orientation of $(OH)^2$ of D-galactopyranose changes from α to β, D-talopyranose is obtained. But, the distance between the O atom in $(OH)^2$ and that in C^6–O bond in $(CH_2OH)^{5\beta.ga}$ is too large to give rise to any influence of the orientation-change of $(OH)^2$ on the internal conformation of C^6–O bond. Therefore, the orientation of OH group in $(CH_2OH)^{5\beta}$ as regards the aldopyranose-ring may be definite and similar in these two sugars in aqueous solutions.

*10 "ma" means the internal conformation concerning $(CH_2OH)^{5\beta}$ in the molecule of D-mannopyranose in aqueous solution. Accordingly, $(CH_2OH)^{5\beta.ma}$ means CH_2OH group which combines with 5-position of the aldopyranose-ring in β-orientation, and at the same time, the internal conformation of the C^6–O bond in this CH_2OH group is of mostly *trans* type and sometimes *gauche* II type. (There exists an equilibrium between these two types). Concerning this information, refer to the previous paper 4.

a) F. J. Bates and associates, "Polarimetry, Saccharimetry and the Sugars", United States Government Printing Office, Washington (1942), p. 762.—"Isbell and Pigman Table of Optical Rotation and Mutarotation of the Reducing Sugars."

*11 "ga" means the internal conformation concerning $(CH_2OH)^{5\beta}$ in the molecule of D-galactopyranose in aqueous solution (cf. *10).

*12 This is $[M]_D^{20}$(W) of α-L-arabinose·$CaCl_2$·$4H_2O$ and not of the pure α-L-arabinose (ref. a)). In order to avoid this defect, it is advisable to use Hudson's data (ref. b)) subsidiarily. ($[M]_D^{20}$(W) of β-L-arabinose=303.3°; $[M]_D^{20}$(W) of α-L-arabinose =133.6°. By using these Hudson's data, An. Diff. of L-arabinose is (303.3−133.6=169.7). This is very consistent with that, obtained by using Isbell and Pigman's data, (286.1−115.6=170.5).

b) E. Montogomery and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 2074 (1934).

c) Landolt-Börnstein, Physikalisch-Chemische Tabellen, Hw. II. p. 985.

d) Values obtained by Ramakrishna-Rao; see Landolt-Börnstein, Physikalisch-Chemische Tabellen, 5th Ed., Eg. II. p. 91.

*13 As the rotatory parameter, g, in the theoretical formula (ref. *14) contains the term, $1/R^3_{ik}$, the former is very sensitive to the magnitude of R_{ik}. In other words, a small deviation in the position of the optical center of a unit group causes a great deviation in $[\mu]^{20}_{Dcalcd}$, with which this unit group is concerned. Then, concerning the position of the optical

of the aqueous solutions of aldopyranoses under question are presumed to be nearly equal (1.34)*16.

Method Proposed

Recently, the author proposed a possible method of estimating the approximate value of the molecular rotation $[M]^{20}_{D}$(W) of a glucide. The principle of this method is to calculate the partial molecular rotation, $[\mu]^{20}_{D\text{calcd}}$ (or $[\mu]^{20}_{D\text{calcd}}(3/n^2+2)$, for convenience), according to Kirkwood's polarizability theory at first, and next, to multiply this calculated value with a definite coefficient which can be obtained by using experimental data of some glucides, to get the true partial molecular rotation, $[\mu]^{20}_{D\text{obs}}$. By summing up all of these possible $[\mu]^{20}_{D\text{obs}}$ in a molecule, we can get the calculated value of $[M]^{20}_{D}$(W) of this substance*17. This method has its ground on the following equation

$$[\mu]^{20}_{D\text{obs}} = \kappa[\mu]^{20}_{D\text{calcd}}, \qquad (1)$$

where κ is a proportionality-constant and is always positive, and Eq. 1 is derived from the formerly presented equation

$$[M]^{20}_{D\text{obs}} = \kappa[M]^{20}_{D\text{calcd}}*18$$

At any rate*19, a multiplying coefficient κ was found important to perform the semi-empirical application of Kirkwood's theory. But now, it seems appropriate to use a new auxiliary coefficient ζ*21, as below; In the case of the dynamical coupling between two unit groups, A and B, it is assumed that κ is the product of two coefficients, ζ_A and ζ_B, which are derived from the groups *A* and *B*, respectively. This is expressed in the following equation

$$\kappa = \zeta_A\zeta_B\text{*22,*23}. \qquad (2)$$

Then, from Eqs. 1 and 2,

$$[\mu]^{20}_{D\text{obs}} = \zeta_A\zeta_B[\mu]^{20}_{D\text{calcd}} \qquad (3)\text{*24}$$

center, a special precaution should be taken. In some of his calculations, Kirkwood located the optical center of a unit group at its center of mass. This manner of treatment was used even in the case of CH_3 group which combines with the three-membered ring in 2,3-epoxybutane (ref. 7). On the other hand, from the standpoint of bond-interaction, Murakami located the optical center of a bond at its center of mass (ref. 8). According to Murakami's treatment, OH group which combines with the aldopyranose-ring is to be divided into ^{r}C—O*15 and O—H bonds. But, on account of lack of data for these two bonds, we were forced to treat OH group as a single particle (ref. *11 in the previous paper 2 and *1 in this article). However, the contribution of ^{r}C—O bond (strictly speaking, σ orbitals of ^{r}C- and O-atoms in this bond) to the degree of polarization of ^{r}C—O—H system, is far greater than that of O—H bond. Then, it may be appropriate to locate the optical center of this system (generally speaking, the optical center of OH group) between ^{r}C- and O-atoms (or at the center of mass of ^{r}C—(OH) bond, for convenience). Analogously, the optical center of $(CH_2OH)^{5\beta}$ is to be placed at the weighed center of the system of C^5—C^6, C^6—(OH), and two C^6—H bonds, that is to say, in the vicinity of C^6-atom.

*14 Ref. "Theoretical Formulae" in the previous paper 2.

7) W. W. Wood, W. Fickett and J. G. Kirkwood, *J. Chem. Phys.*, **20**, 561 (1952).

8) H. Murakami, This Bulletin, **27**, 246 (1954); **28**, 583 (1955).

*15 ^{r}C-atom means the C atom which constitutes the aldopyranose-ring.

*16 Ref. *8 in the previous paper 1.

*17 Ref. "Method Proposed." in the previous paper 3. This method is called "Polarizability-Multiplying method (or abbreviated to PM-method)" by the author, hereafter.

*18 Eq. 4 in the previous paper 2.

*19 It has already been demonstrated that, in the calculation of the optical rotatory power by Kirkwood's polarizability theory, a small deviation in atomic distance or in valency angles causes only a small deviation in the calculated value of optical rotatory power. (ref. *7 in the previous paper 2). Then, the comparatively large value of κ, $(12.37/n^2+2)$*20, can not be due to the imperfectness of the molecular model, used for calculation. It may be due either to the inadequate location of the optical center of OH group, or to the changes of the values of $\alpha_i\beta_i$ or $\alpha_k\beta_k$ in the theoretical formula (ref. *14) which are caused by solvation (ref. *13 in the previous paper 2).

*20 Ref. "Method Proposed" in the previous paper 1.

*21 The author chose ζ, a Greek letter which corresponds to *z*, to represent the new coefficient. Thus, the notations in PM-method, X, Λ and ζ were suggested by x, y and *z*. (ref. *10 in the previous paper 3).

*22 From the viewpoint of its physical meaning, ζ should be always positive.

*23 The proportionality constant κ was suggested by the Murakami's report (8) on the study of polypeptides of alanine. But here, κ loses its original physical meaning, and the physical meaning of κ is specified in such a way that its value changes when one of two unit groups, A or B, changes.

*24 As was already described in the previous paper 3, the following equation is given in the case of the dynamical coupling of two OH groups,

$$[\mu]^{20}_{D\text{obs}} = 4.123[\mu]^{20}_{D\text{calcd}}(3/n^2+2)$$

In this case,

$$\kappa = \zeta^2_{OH} = 4.123(3/n^2+2)$$
$$\therefore\ \zeta_{OH} = 2.0305(3/n^2+2)^{1/2}$$

TABLE II

$[\mu]^{20}_{D\text{calcd}}(3/n^2+2)$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT $(CH_2OH)^{5\beta}$ AND RING) IN MC DONALD AND BEEVERS' MOLECULAR MODEL

	4β	4α	3β	3α	2β	2α
1α	−0.06 (−0.13)	−0.05 (−0.03)	2.23 (1.76)	0.52 (0.45)	1.31 (0.68)	10.62 (5.96)
1β	−0.29 (−0.20)	0.25 (0.14)	0.21 (0.10)	−2.33 (−1.85)	11.86 (6.81)	−12.97 (−7.59)
2α	1.48 (1.38)	0.51 (0.27)	12.47 (7.23)	−10.11 (−5.59)		
2β	0.17 (0.17)	−2.04 (−1.66)	−11.96 (−7.04)	−1.26 (−0.64)		
3α	0.93 (0.48)	10.76 (5.83)				
3β	11.58 (6.59)	−11.97 (−6.57)				

The values, calculated by supposing that the optical center of OH group is located at its O atom, are given in parentheses.

TABLE III

$[\mu]^{20}_{D\text{calcd}}(3/n^2+2)$, CAUSED BY THE DYNAMICAL COUPLING EFFECT OF $(OH)^1$ IN D-GLUCOPYRANOSE

	2α	3β	4α	5β.ma	R
1α	10.62	2.23	−0.05	$(1\alpha)\times(5\beta.\text{ma})$ *26	$(1\alpha)\times R$
1β	−12.97	0.21	0.25	$(1\beta)\times(5\beta.\text{ma})$	$(1\beta)\times R$

TABLE IV

$[\mu]^{20}_{D\text{obs}}(3/n^2+2)$, CAUSED BY THE DYNAMICAL COUPLING EFFECT OF $(OH)^1$ IN D-GLUCOPYRANOSE

	2α	3β	4α	5β.ma	R
1α	$10.62\zeta^2_{OH}$ *27	$2.23\zeta^2_{OH}$	$-0.05\zeta^2_{OH}$	$\{(1\alpha)\times(5\beta.\text{ma})\}\zeta_{OH}\zeta_{CH_2OH}$	$\{(1\alpha)\times R\}\zeta_{OH}\zeta_R$
1β	$-12.97\zeta^2_{OH}$	$0.21\zeta^2_{OH}$	$0.25\zeta^2_{OH}$	$\{(1\beta)\times(5\beta.\text{ma})\}\zeta_{OH}\zeta_{CH_2OH}$	$\{(1\beta)\times R\}\zeta_{OH}\zeta_R$

On the other hand, $[\mu]^{20}_{D\text{calcd}}$, caused by the dynamical coupling effect between any two members of unit groups (except $(CH_2OH)^{5\beta}$ and ring) in the aldopyranose-molecule, can be calculated by using the theoretical formulae*14. The results of calculation are shown in Table II. Then, $[\mu]^{20}_{D\text{calcd}}(3/n^2+2)$ and $[\mu]^{20}_{D\text{obs}}(3/n^2+2)$, caused by the dynamical coupling effects between $(OH)^1$*25 and the other unit groups in D-glucopyranose are as shown in Tables III and IV, respectively. Now, $[\mu]^{20}_{D\text{obs}}$ of An. Diff.*3 of D-glucopyranose is as follows;

$$
\begin{aligned}
&[10.62\zeta^2_{OH}+2.23\zeta^2_{OH}-0.05\zeta^2_{OH}\\
&\quad+\{(1\alpha)\times(5\beta.\text{ma})\}\zeta_{OH}\zeta_{CH_2OH}\\
&\quad+\{(1\alpha)\times R\}\zeta_{OH}\zeta_R](n^2+2/3)\\
&\quad-[-12.97\zeta^2_{OH}+0.21\zeta^2_{OH}+0.25\zeta^2_{OH}\\
&\quad+\{(1\beta)\times(5\beta.\text{ma})\}\zeta_{OH}\zeta_{CH_2OH}\\
&\quad+\{(1\beta)\times R\}\zeta_{OH}\zeta_R](n^2+2/3)\\
&\quad=(25.31\zeta^2_{OH}+A+B)(n^2+2/3)
\end{aligned}
$$

where

$$A\equiv\{(1\alpha)\times(5\beta.\text{ma})-(1\beta)\times(5\beta.\text{ma})\}\zeta_{OH}\zeta_{CH_2OH} \quad (4)$$

$$B\equiv\{(1\alpha)\times R-(1\beta)\times R\}\zeta_{OH}\zeta_R \quad (5)$$

The corresponding observed value is given by, $\{[M]^{20}_D(W)$ of α-D-glucose$\}$ minus $\{[M]^{20}_D(W)$ of β-D-glucose$\}$. This is $(202.1-33.7)$*28$=168.4$. Of course, this observed value should be equal to its corresponding $[\mu]^{20}_{D\text{obs}}$. Then,

$$168.4=(25.31\zeta^2_{OH}+A+B)(n^2+2/3) \quad (6)$$

By using the method like that mentioned above, three other equations are obtained. From D-mannopyranose,

$$83.4=(-8.83\zeta^2_{OH}+A+B)(n^2+2/3) \quad (7)$$

This is ζ-coefficient of OH group in the aldopyranose-molecule of C 1 conformation in aqueous solution, calculated by using the ideal model and Riiber's data of $[M]^{20}_D(W)$, supposing that the optical center of (OH) group is located at its O atom. This value of ζ_{OH} is nearly equal to that, obtained by using Mc Donald and Beevers' model and Isbell and Pigman's data of $[M]^{20}_D(W)$, supposing that the optical center of OH group is at its O atom. (ref. *44 in this article.)

*25 $(OH)^1$ means OH group, which combines with 1-position of the ring, and so on.

*26 $(5\beta.\text{ma})$ is an abbreviated symbol of $(CH_2OH)^{5\beta.\text{ma}}$, and so on.

*27 Eq. 3 is used, here.

*28 Ref. Table 1 in this article.

From D-galactopyranose,

$$176.4 = (25.84\zeta_{OH}^2 + A' + B)(n^2+2/3) \quad (8)$$

and from L-arabinopyranose,

$$170.5 = (25.84\zeta_{OH}^2 + B)(n^2+2/3) \quad (9)^{*29}$$

where

$$A' \equiv \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\}\zeta_{OH}\zeta_{CH_2OH} \quad (10)$$

From Eq. 6 minus 7,

$$85.0 = 34.14\zeta_{OH}^2(n^2+2/3)$$

$$\therefore \quad \zeta_{OH}^2 = 2.4897(3/n^2+2) \quad (11)$$

$$\text{or} \quad \zeta_{OH} = 1.5779(3/n^2+2)^{1/2} \quad ^{*22,*30} \quad (12)$$

From Eqs. 6 and 11,

$$106.2 = B(n^2+2/3) = \{(1\alpha)\times R - (1\beta)\times R\}\zeta_{OH}\zeta_R(n^2+2/3)^{*31} = (1\alpha)\,\text{Å}\,R - (1\beta)\,\text{Å}\,R \quad (13)^{*32,*29}$$

from Eqs. 6, 11 and 13,

$$-0.8 = A(n^2+2/3) = \{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\}\zeta_{OH}\zeta_{CH_2OH}(n^2+2/3)^{*33,*35}$$

$$\therefore \quad \zeta_{OH}\zeta_{CH_2OH}(n^2+2/3) = -0.8/\{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} \quad (14)$$

and from Eq. 8 minus 9,

$$5.9 = A'(n^2+2/3) = \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\}\zeta_{OH}\zeta_{CH_2OH}(n^2+2/3)\}^{*34}$$

$$\therefore \quad \zeta_{OH}\zeta_{CH_2OH}(n^2+2/3) = 5.9/\{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} \quad (15)$$

As each of ζ_{OH}, ζ_{CH_2OH} and $(n^2+2/3)$ in Eqs. 14 and 15 is always positive (ref. *22), the following two inequalities are obtained. From Eq. 14,

$$\{(1\alpha)\times(5\beta\cdot\mathrm{ma}) - (1\beta)\times(5\beta\cdot\mathrm{ma})\} < 0 \quad \text{(Ineq. 1)}$$

From Eq. 15,

$$\{(1\alpha)\times(5\beta\cdot\mathrm{ga}) - (1\beta)\times(5\beta\cdot\mathrm{ga})\} > 0 \quad \text{(Ineq. 2)}$$

The left-hand side of Eq. 14 is equal to that of Eq. 15, then the right-hand sides of these two equations should be equal to each other,

$$-0.8/\{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} = 5.9/\{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\}$$

$$\therefore \quad \{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} / \{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\} = -7.38 \quad (16)$$

Eq. 16 indicates that

$$\{(1\alpha)\times(5\beta.\mathrm{ga}) - (1\beta)\times(5\beta.\mathrm{ga})\} \neq \{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma})\}$$

$$\therefore \quad 5\beta.\mathrm{ga} \neq 5\beta.\mathrm{ma} \quad (17)^{*36}$$

Now, in order to simplify the following calculations, two simplifications are made as below;

(Simp. I) The internal conformation of C^6—O bond in D-mannopyranose in aqueous solution is only of *trans* type. (ref. *10). Shortly speaking,

$$5\beta.\mathrm{ma} = 5\beta.t^{*37}$$

(Simp. II) The internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is one of the *trans*, *gauche* I or *gauche* II types*38, and this type is represented by x. Then,

$$5\beta\cdot\mathrm{ga} = 5\beta\cdot\mathrm{x}$$

*29 Cf. *35 in this article.

*30 If D-talopyranose has C 1 conformation (ref. *8), it is possible to calculate ζ_{OH} by using $[M]_D^{20}(W)$ of D-galactose and of D-talose. The calculated value of ζ_{OH} in this case, is 1.5086 $(3/n^2+2)^{1/2}$. This is nearly equal to the value in Eq. 12.

*31 Eq. 5 is used, here.

*32 When the partial molecular rotation is caused by the dynamical coupling effect between unit groups A and B,

$$[\mu]_{D\,obs}^{20} = \zeta_A\zeta_B[\mu]_{D\,calcd}^{20}$$

(Eq. 3 in this article), where

$$[\mu]_{D\,obs}^{20} = (A)\,\text{Å}\,(B)$$

(ref. *10 in the previous paper 3), and

$$[\mu]_{D\,calcd}^{20} = \{(A)\times(B)\}(n^2+2/3)$$

(ref. *14 in the previous paper 2). Then,

$$(A)\,\text{Å}\,(B) = \{(A)\times(B)\}\zeta_A\zeta_B(n^2+2/3). \quad (32)$$

*33 Eq. 4 is used, here.

*34 Eq. 10 is used, here.

*35 When using Hudson's data of L-arabinoses (ref. *12 in this article),

$$169.7 = (25.84\zeta_{OH}^2 + B)(n^2+2/3) \quad (9)^*$$

$$105.4 = (1\alpha)\,\text{Å}\,R - (1\beta)\,\text{Å}\,R \quad (13)^*$$

$$\{(1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times 5\beta.\mathrm{ma})\}\zeta_{OH}\zeta_{CH_2OH}(n^2+2/3) = 0$$

$$\text{or} \quad (1\alpha)\times(5\beta.\mathrm{ma}) - (1\beta)\times(5\beta.\mathrm{ma}) = 0 \quad (14)^*$$

*36 Strictly speaking, as each of 5β.ga and 5β.ma seems to be the mixture of two types of internal conformation of C^6—O bond (ref. *10), Eq. 17 shows that the quantitative ratio of two types of internal conformation of C^6—O bond is entirely different in D-galactopyranose and in D-mannopyranose in their aqueous solutions.

*37 $5\beta.t$ is an abbreviated symbol of $5\beta.trans$.

*38 cf. Fig. 2 in the previous paper 4.

By using these two simplifications, the following two inequalities and two equations are obtained.

From Ineq. 1,

$$\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}<0 \quad \text{(Ineq. 1')}$$

From (Ineq. 2),

$$\{(1\alpha)\times(5\beta.\mathrm{x})-(1\beta)\times(5\beta.\mathrm{x})\}>0 \quad \text{(Ineq. 2')}$$

From Eq. 17,

$$5\beta\cdot\mathrm{x}\neq 5\beta\cdot t \qquad (17')^{*39}$$

and from Eq. 16,

$$\{(1\alpha)\times(5\beta.\mathrm{x})-(1\beta)\times(5\beta.\mathrm{x})\}/\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}=-7.38 \qquad (16')$$

Next, the value of $\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}$ was calculated as a function of the angle θ[*2] which defines the direction of the optical axis of CH_2OH group. The results of calculation are given in the second column of Table V.

TABLE V

$[\mu]_{\mathrm{D}}^{20}{}_{\mathrm{calcd}}(3/n^2+2)$-DIFFERENCE AS A FUNCTION OF θ, CALCULATED BY USING MC DONALD AND BEEVERS' MODEL

θ	Diff (t)	Diff (gI)	Diff (gII)	Diff (gII) /Diff (t)
0°	9.90			
10°	8.21			
20°	5.80			
30°	2.95			
36°	1.18			
40°	0.02			
40°05′	−0.01	−16.54	4.72	−472.00
40°10′	−0.03	−16.52	4.69	−156.33
41°	−0.27	−16.33	4.42	−16.37
41°50′	−0.51	−16.11	4.16	−8.16
42°	−0.55	−16.07	4.09	−7.44
42°10′	−0.60	−16.02	4.04	−6.73
43°	−0.82	−15.79	3.77	−4.60
50°	−2.65	−13.51	1.21	−0.46
54°44′	−3.73	−11.61	−0.66	0.18

Diff (t) ·····$\{(1\alpha)\times(5\beta\cdot t)-(1\beta)\times(5\beta\cdot t)\}$
Diff (g I)·····$\{(1\alpha)\times(5\beta\cdot g\,\mathrm{I})-(1\beta)\times(5\beta\cdot g\,\mathrm{I})\}$
Diff (g II) ···$\{(1\alpha)\times(5\beta\cdot g\,\mathrm{II})-(1\beta)\times(5\beta\cdot g\,\mathrm{II})\}$

Combining these values with (Ineq. 1'), the following conclusion is obtained,

$$40°05' \leqq \theta \leqq 54°44'$$

In order to examine *gauche* I type, the value of $\{(1\alpha)\times(5\beta.g\,\mathrm{I})$[*40] $-(1\beta)\times(5\beta.g\,\mathrm{I})\}$ was calculated as a function of θ which lies between 40°05′ and 54°44′. The results of calculation are given in the third column in Table V. But these values of $\{(1\alpha)\times(5\beta.g\ 1)-(1\beta)\times(5\beta.g\ 1)\}$ are all negative. Then, by referring Ineq. 2′, it is concluded that

$$5\beta.g\,1\neq 5\beta.\mathrm{x} \qquad (18)^{*41}$$

Combining Eqs. 17′ and 18 with (Simp. II),

$$5\beta\cdot\mathrm{ga}=5\beta\cdot\mathrm{x}=5\beta\cdot g\,\mathrm{II} \qquad (19)$$

Consequently, the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is of *gauche* II type[*42]. Then, Eq. 16′ becomes as below;

$$\{(1\alpha)\times(5\beta.g\,\mathrm{II})-(1\beta)\times(5\beta.g\,\mathrm{II})\}/\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}=-7.38. \qquad (16'')$$

In order to find the suitable value of θ which satisfies Eq. 16″, the value of the left side of this equation was calculated as a function of θ. The results of the calculation are given in the fifth column of Table V, and the value, −7.38, of

$$\{(1\alpha)\times(5\beta.g\,\mathrm{II})-(1\beta)\times(5\beta.g\,\mathrm{II})\}/\{(1\alpha)\times(5\beta.t)-(1\beta)\times(5\beta.t)\}$$

can be found at $\theta\simeq 42°$[*43].

It is also apparent in Table V that the value of $\{(1\alpha)\times(5\beta.g\,\mathrm{II})-(1\beta)\times(5\beta.g\,\mathrm{II})\}$ which corresponds to the above-found value of θ is 4.09. When this value, Eqs.

*39 Concretely speaking, the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is not of *trans* type.

*40 $5\beta.g\mathrm{I}$ is an abbreviated symbol of $5\beta.$*gauche* I, and so on.

*41 Concretely speaking, the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is not of *gauche* I type.

*42 This conclusion coincides with that obtained from the viewpoint of the atomic distances between the O atom in $(CH_2OH)^{5\beta}$ (i. e. O^6-atom) and the neighboring atoms. (ref. "Discussion on the Results." in the previous paper 4). The distance between O^6- and $O^{4\beta}$-atoms in D-galactopyranose are as below; *trans* (3.49 Å), *gauche* I (4.16 Å), *gauche* II (2.69 Å) Then, the distance between O^6- and $O^{4\beta}$-atoms in *gauche* II form is the shortest and is equal to the length of a hydrogen bond. Therefore, the movable atom O^6 would be attracted by $O^{4\beta}$-atom and be forced to rest at *gauche* II position.

*43 The value, 0, of

$$\{(1\alpha)\times(5\beta.\mathrm{ma})-(1\beta)\times(5\beta.\mathrm{ma})\}=\mathrm{Diff}(t),$$

(ref. Eq. 14* in *35) is found at $\theta\simeq 40°05'$ in Table V, and its corresponding Diff (g II) is 4.72. Accordingly,

$$\zeta_{CH_2OH}=0.7922(3/n^2+2)^{1/2} \qquad (20)^*$$

These are the values concerning $(CH_2OH)^{5\beta}$, calculated by using Hudson's data of L-arabinoses. (ref. *12).

19 and 12 are used, Eq. 15 becomes as below;

$$1.5779(3/n^2+2)^{1/2}\zeta_{CH_2OH}(n^2+2/3)=5.9/4.09$$
$$\therefore\ \zeta_{CH_2OH}=0.9142(3/n^2+2)^{1/2}\ *43,*44 \qquad (20)$$

Conclusion

The results of calculation in this paper are as follows:

(1) If the internal conformation of C^6—O bond in D-galactopyranose in aqueous solution is only one of the *trans*, *gauche* I or *gauche* II types, it should be of *gauche* II type.

(2) It is expected that the optical axis of $(CH_2OH)^{5\beta}$ is placed on the plane of C^5-atom and its C^6—O bond, and this optical axis inclines to the C^6—O bond at 42°*43.

(3) ζ-coefficients of OH and CH_2OH groups, in this case, are $1.5779(3/n^2+2)^{1/2}$ and $0.9142(3/n^2+2)^{1/2}$ *43, respectively.

The author wishes to express his sincere thanks to Professor S. Tanaka of Kyoto University for his valuable discussion and encouragement throughout the course of this study. Also the author wants to express his great thanks to the members of the Editorial Board of this Bulletin for their helpful suggestion concerning the importance of the position of the optical center of the unit group.

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*44 For comparison, the values, calculated by supposing that the optical center of OH group is located at O atom and that of CH_2OH group is at its center of mass (ref. *13), are given here;

	Isbell and Pigman's data of L-arabinoses	Hudson's data of L-arabinoses
ζ_{OH}	$2.0782(3/n^2+2)^{1/2}$	$2.0782(3/n^2+2)^{1/2}$
ζ_{CH_2OH}	$3.5049(3/n^2+2)^{1/2}$	$3.3936(3/n^2+2)^{1/2}$
θ	34°50′	34°20′

Molecular Rotations of Glucides in Relation to their Structures. VI. Optical Superposition in Methyl Pentoses.[*1] *Presumption of Two Unknown* $[M]_D^0$(W)

Shukichi YAMANA

(Received December 26, 1957)

Recently, the author discussed $[M]_D^{20}$(W) of pentoses by using PM-method*2, and concluded that the principle of optical superposition of Kirkwood's idea exists in this group[2]. In this paper, the author tries to investigate whether this principle exists in methyl pentoses by using the same method.

Molecular Model and Data Used

The names of pentoses and methyl pentoses to which the calculations were applied, with groups in their molecules, and their corresponding molecular rotations are tabulated in Table I.

These pentoses and methyl pentoses except α-D- and β-D-isorhamnoses were concluded to have C 1 conformation by Reeves' experiments of cuprammonium-glycoside complexes[3]*4. It is presumed

*1 Only the glucides which have the six-membered (pyranose) ring in their molecules, are treated in this article, and so the suffix "-pyranose" of their names is omitted, here.

*2 Ref.*17 in the previous paper 1.

1) S. Yamana, This Bulletin, **31**, 558 (1958).

2) S. Yamana, ibid. **30**, 916 (1957).

*3 Hudson's data is 303.3° (ref. *12 in the previous paper 1).

a) F. J. Bates and Associates, "Polarimetry, Saccharimentry and the Sugars", United States Government Printing Office, Washington (1942), p. 762.

b) ibid. p. 750.

c) ibid. p. 726.

3) R. E. Reeves, *J. Am. Chem. Soc.*, **72**, 1499 (1950).

TABLE I

Name	Unit Groups	$[M]_D^{20}$(W)	Lit.
α-D-xylose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, Ring]	140.5°	(a)
β-L-arabinose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	286.1°*3	(a)
α-D-rhamnose	[$(OH)^{1\alpha}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]	15.7°	(a)
β-D-rhamnose	[$(OH)^{1\beta}$, $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]	−63.0°	(b)
α-D-isorhamnose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]	120.3°	(c)
β-D-isorhamnose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$, Ring]		
α-D-fucose	[$(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_3)^{5\beta}$, Ring]	251.0°	(a)
β-D-fucose	[$(OH)^{1\beta}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_3)^{5\beta}$, Ring]		

TABLE II

$[\mu]_{D^{obs}}^{20}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING) IN McDONALD AND BEEVERS' MOLECULAR MODEL (WHEN THE OPTICAL CENTER OF (OH) GROUP IS LOCATED AT THE CENTER OF MASS OF $^{\alpha}C$—(OH) BOND, AND THAT OF $(CH_3)^{5\beta}$ GROUP IS AT THE CENTER OF MASS OF C^5—$(CH_3)^{5\beta}$ BOND)

	$(CH_3)^{5\beta}$	4β	4α	3β	3α	2β	2α
1α	−2.0 (−4.2)	−0.1	−0.1	5.6	1.3	3.3	26.4
1β	0.4 (0.8)	−0.7	0.6	0.5	−5.8	29.5	−32.3
2α	−0.3 (−0.5)	3.7	1.3	31.0	−25.2		
2β	0.2 (0.4)	0.4	−5.1	−29.8	−3.1		
3α	1.5 (3.2)	2.3	26.8				
3β	−0.6 (−1.2)	28.8	−29.8				
4α	7.3 (15.7)						
4β	−7.6 (−16.4)						

Note: The values of $[\mu]_{D^{obs}}^{20}$ concerning $(CH_3)^{5\beta}$, calculated from Hudson's data of β-L-arabinose (ref. *3), are given in parentheses.

TABLE III

$[\mu]_{D^{obs}}^{20}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS (EXCEPT RING) IN McDONALD AND BEEVERS' MOLECULAR MODEL (WHEN THE OPTICAL CENTER OF (OH) GROUP IS LOCATED AT O ATOM, AND THAT OF $(CH_3)^{5\beta}$ GROUP IS AT C ATOM)

	$(CH_3)^{5\beta}$	4β	4α	3β	3α	2β	2α
1α	−2.7 (−5.7)	−0.6	−0.1	7.6	1.9	2.9	25.7
1β	0.4 (0.8)	−0.9	0.6	0.4	−8.0	29.4	−32.8
2α	−0.3 (−0.6)	6.0	1.2	31.2	−24.1		
2β	0.2 (0.5)	0.7	−7.2	−30.4	−2.8		
3α	2.0 (4.4)	2.1	25.2				
3β	−0.5 (−1.1)	28.5	−28.4				
4α	7.3 (15.7)						
4β	−7.6 (−16.4)						

Note: The values of $[\mu]_{D^{obs}}^{20}$ concerning $(CH_3)^{5\beta}$, calculated from Hudson's data of β-L-arabinose (ref. *3), are given in parentheses.

that α-D- and β-D-isorhamnoses have also C 1 conformation because their corresponding aldohexoses(α-D- and β-D-glucoses) were determined to have C 1 conformation. McDonald and Beevers' molecular model, used in the previous papers 1 and 4, is used again in this article. The optical data for OH group and H atom, used in the previous paper 1, are also employed without any correction. It is supposed that CH_3 group has its optical axis of cylindrical symmetry directed along its bond to the atom with which it combines*5 and the optical center of $(CH_3)^{5\beta}$ group is located at the center of mass of C^5—$(CH_3)^{5\beta}$ bond*6. Values of mean polarizability α and of anisotropy ratio β of CH_3 group are 2.27×10^{-24}(cc)[d] and 0.35[e] respectively. The refractive indices of the aqueous solutions of pentoses and methyl pentoses under question are presumed to be nearly equal (1.34)*7.

Method Proposed

If the orientation of $(OH)^4$ in α-D-fucose changes from β to α, α-D-isorhamnose is obtained*8,*9. Therefore, it is appropriate to treat $[M]^{20}_D$(W)-change, caused by the orientation-change of $(OH)^4$*10 in these two sugars at first. The unit groups which can couple with $(OH)^4$ dynamically in α-D-fucose, are $(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(CH_3)^{5\beta}$ and Ring*8. Then, $\sum[\mu]^{20}_{Dobs}$, caused by the dynamical coupling effect of $(OH)^4$ in α-D-fucose, is given by the following equation,

$$(4\beta)\,\Lambda\{(1\alpha)+(2\alpha)+(3\beta)+(CH_3)^{5\beta}+R\}^{*11}$$
$$=(4\beta)\,\Lambda\,(1\alpha)+(4\beta)\,\Lambda\,(2\alpha)+(4\beta)\,\Lambda\,(3\beta)$$
$$+(4\beta)\,\Lambda\,(CH_3)^{5\beta}+(4\beta)\,\Lambda R\equiv E$$

In the same way, the value in α-D-isorhamnose is as below,

$$(4\alpha)\,\Lambda\{(1\alpha)+(2\alpha)+(3\beta)+(CH_3)^{5\beta}+R\}$$
$$=(4\alpha)\,\Lambda\,(1\alpha)+(4\alpha)\,\Lambda\,(2\alpha)+(4\alpha)\,\Lambda\,(3\beta)$$
$$+(4\alpha)\,\Lambda\,(CH_3)^{5\beta}+(4\alpha)\,\Lambda R\equiv F$$

Accordingly, $[\mu]^{20}_{Dobs}$-change, caused by the orientation-change of $(OH)^4$ in α-D-fucose from β to α (that is to say, $[\mu]^{20}_{Dobs}$ of Yo. Diff. among α-D-isorhamnose and α-D-fucose), is $(F-E)$. The corresponding observed value is given by, {$[M]^{20}_D$(W) of α-D-isorhamnose} minus {$[M]^{20}_D$(W) of α-D-fucose}.

This is $(120.3-251.0)^{*8}=-130.7$. As these two values should be equal to each other,

$$-130.7=\text{Yo. Diff.}=(F-E)=\{(4\alpha)\,\Lambda\,(1\alpha)$$
$$+(4\alpha)\,\Lambda\,(2\alpha)+(4\alpha)\,\Lambda\,(3\beta)+(4\alpha)\,\Lambda\,(CH_3)^{5\beta}$$
$$+(4\alpha)\,\Lambda R\}-\{(4\beta)\,\Lambda\,(1\alpha)+(4\beta)\,\Lambda\,(2\alpha)$$
$$+(4\beta)\,\Lambda\,(3\beta)+(4\beta)\,\Lambda\,(CH_3)^{5\beta}+(4\beta)\,\Lambda R\}$$
$$(1)^{*12}$$

By using the method similar to that mentioned above, the following equation is obtained from Yo. Diff. among α-D-xylose and β-L-arabinose.

$$\{(4\alpha)-(4\beta)\}\,\Lambda\{(1\alpha)+(2\alpha)+(3\beta)+R\}$$
$$=\{(4\alpha)\,\Lambda\,(1\alpha)+(4\alpha)\,\Lambda\,(2\alpha)+(4\alpha)\,\Lambda\,(3\beta)$$
$$+(4\alpha)\,\Lambda R\}-\{(4\beta)\,\Lambda\,(1\alpha)+(4\beta)\,\Lambda\,(2\alpha)$$

*4 There are sixteen kinds of methyl pentose of D-series and the conformations of α-D- and β-D-rhamnoses and of α-D- and β-D-fucoses have been decided. But, the rest of them have not yet been determined.

4) S. Yamana, This Bulletin, **30**, 920 (1957).

*5 This is C^5-atom, in this case (ref. Fig. 1 in the previous paper 4).

*6 cf. *13 in the previous paper 1.

d) Landolt-Börnstein,"Physikalisch-Chemische Tabellen", Hw. II, p. 985.

e) Values obtained by Cabannes and Granier; see Landolt-Börnstein, " Physikalisch-Chemische Tabellen", 5th Ed. Eg. II, p. 90.

*7 Ref. *8 in the previous paper 5.

5) S. Yamana, This Bulletin, **30**, 207 (1957).

*8 Ref. Table I in this article.

*9 Generally, the diastereomer at C^1-atom is called " anomer " and that at C^2-atom is called " epimer " (ref. 6). Now, the author proposes to use the names of " miner [mi:mə] " and " yomer [jɔ:mə] " to represent the diastereomers at C^3- and C^4-atoms, respectively. " mi- " and " yo- " mean 3 and 4 in Japanese, respectively. The reason for using the oriental language and not European in this case, is to avoid their confusion with the names of polymers (" trimer " etc.). Then, it can be said that α-D-fucose and α-D-isorhamnose are " yomer " to each other.

6) Tollens-Elsner, " Kurzes Handbuch der Kohlenhydrate", Johann Ambrosius Barth, Verlag Leipzig (1935), p. 16, 20.

*10 This is called " yomeric difference (or abbreviated to Yo. Diff.) " by the author (ref. *9 in this article cf. *3 in the previous paper 1).

*11 Ref. *10 in the previous paper 2.

*12 The right side of Eq. 1 can be rewritten as below,

$$\{(4\alpha)\,\Lambda\,(1\alpha)+(4\alpha)\,\Lambda\,(2\alpha)+(4\alpha)\,\Lambda\,(3\beta)$$
$$+(4\alpha)\,\Lambda\,(CH_3)^{5\beta}+(4\alpha)\,\Lambda R\}-\{(4\beta)\,\Lambda\,(1\alpha)$$
$$+(4\beta)\,\Lambda\,(2\alpha)+(4\beta)\,\Lambda\,(3\beta)+(4\beta)\,\Lambda\,(CH_3)^{5\beta}$$
$$+(4\beta)\,\Lambda R\}=(4\alpha)\,\Lambda\{(1\alpha)+(2\alpha)+(3\beta)$$
$$+(CH_3)^{5\beta}+R\}-(4\beta)\,\Lambda\{(1\alpha)+(2\alpha)+(3\beta)$$
$$+(CH_3)^{5\beta}+R\}=\{(4\alpha)-(4\beta)\}\,\Lambda\{(1\alpha)+(2\alpha)$$
$$+(3\beta)+(CH_3)^{5\beta}+R\}$$

(∵ the notation Λ can be treated in the same way as the multiplication-symbol × of the algebra.) Then, it can be said that $\{(4\alpha)-(4\beta)\}$ Λ{……} is a formula of $[\mu]^{20}_{Dobs}$ of Yo. Diff.

$$+(4\beta)\,\lambda\,(3\beta)+(4\beta)\,\lambda\,\mathrm{R}\}=-145.6^{*13} \quad (2)$$

From Eq. 1 minus 2,

$$(4\alpha)\,\lambda\,(\mathrm{CH_3})^{5\beta}-(4\beta)\,\lambda\,(\mathrm{CH_3})^{5\beta}=14.9$$

This equation can be rewritten as below*14,

$$\{(4\alpha)\times(\mathrm{CH_3})^{5\beta}-(4\beta)\times(\mathrm{CH_3})^{5\beta}\}$$
$$\zeta_{OH}\zeta_{CH_3}(n^2+2/3)=14.9 \quad (3)^{*13}$$

On the other hand, the value of $(4\alpha)\times(\mathrm{CH_3})^{5\beta}$ and $(4\beta)\times(\mathrm{CH_3})^{5\beta}$ in Eq. 3 can be calculated by using the theoretical formulae*15 as 23.58 and -24.54 respectively. By using these values in Eq. 3,

$$\zeta_{OH}\zeta_{CH_3}=0.3096\ (3/n^2+2) \quad (4)^{*13}$$

But, ζ_{OH} was already calculated and its value is 1.5779 $(3/n^2+2)^{1/2}$*16. Then

$$\zeta_{CH_3}=0.3096(3/n^2+2)/1.5779(3/n^2+2)^{1/2}$$
$$=0.1962(3/n^2+2)^{1/2} \quad (5)^{*17,*18}$$

Thus, ζ-coefficient of CH_3 group which is indispensable in calculation of $[\mu]^{20}_{D\mathrm{obs}}$ concerning CH_3 group, can be obtained quasi-empirically. Next, an attempt has been made to examine whether this value of ζ_{CH_3} is suitable or not, as follows; at first, by combining these values of ζ_{CH_3} and ζ_{OH} with Table II of the previous paper 1, the tables of $[\mu]^{20}_{D\mathrm{obs}}$ in the methyl pentose-molecule can be made*19. They are Tables II and III.

The unit groups which can couple with $(OH)^1$ dynamically in D-rhamnose, are $(OH)^{2\beta}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, $(CH_3)^{5\beta}$ and Ring*8. Then, $\Sigma[\mu]^{20}_{D\mathrm{obs}}$-change, caused by the orientation-change of $(OH)^1$ in this sugar from β to α (that is to say $[\mu]^{20}_{D\mathrm{obs}}$ of An. Diff.*20 of D-rhamnose), is represented as below,

$$\{(1\alpha)-(1\beta)\}\,\lambda\,\{(2\beta)+(3\beta)+(4\alpha)+(\mathrm{CH_3})^{5\beta}+\mathrm{R}\}^{*21}=\{(1\alpha)\,\lambda\,(2\beta)+(1\alpha)\,\lambda\,(3\beta)+(1\alpha)\,\lambda\,(4\alpha)+(1\alpha)\,\lambda\,(\mathrm{CH_3})^{5\beta}+(1\alpha)\,\lambda\,\mathrm{R}\}-\{(1\beta)\,\lambda\,(2\beta)+(1\beta)\,\lambda\,(3\beta)+(1\beta)\,\lambda\,(4\alpha)+(1\beta)\,\lambda\,(\mathrm{CH_3})^{5\beta}+(1\beta)\,\lambda\,\mathrm{R}\}=\{3.3+5.6-0.1-2.0+(1\alpha)\,\lambda\,\mathrm{R}\}-\{29.5+0.5+0.6+0.4+(1\beta)\,\lambda\,\mathrm{R}\}^{*22}=-24.2+(1\alpha)\,\lambda\,\mathrm{R}-(1\beta)\,\lambda\,\mathrm{R}=82.0^{*23,*24}$$

The corresponding observed value is given by, $\{[M]^{20}_{D}(\mathrm{W})$ of α-D-rhamnose$\}$ minus $\{[M]^{20}_{D}(\mathrm{W})$ of β-D-rhamnose$\}$. This is, $15.7-(-63.0)=78.7$.

This observed value is almost consistent with the above calculated value, 82.0. This fact indicates that there exists the principle of optical superposition of Kirkwood's idea in methyl pentoses, and also that the values in Table II are all suitable and accordingly the value of ζ_{CH_3} in Eq. 5 is almost satisfactory. Next, the unknown $[M]^{20}_{D}(\mathrm{W})$ of β-D-fucose is presumed by using the method, similar to that mentioned above.

$[\mu]^{20}_{D\mathrm{obs}}$ of An. Diff. of D-fucose is given by the following equation.

$$\{(1\alpha)-(1\beta)\}\,\lambda\,\{(2\alpha)+(3\beta)+(4\beta)+(\mathrm{CH_3})^{5\beta}+\mathrm{R}\}^{*21}=\{(1\alpha)\,\lambda\,(2\alpha)+(1\alpha)\,\lambda\,(3\beta)+(1\alpha)\,\lambda\,(4\beta)+(1\alpha)\,\lambda\,(\mathrm{CH_3})^{5\beta}+(1\alpha)\,\lambda\,\mathrm{R}\}-\{(1\beta)\,\lambda\,(2\alpha)+(1\beta)\,\lambda\,(3\beta)+(1\beta)\,\lambda\,(4\beta)+(1\beta)\,\lambda\,(\mathrm{CH_3})^{5\beta}+(1\beta)\,\lambda\,\mathrm{R}\}=\{26.4+5.6-0.1-2.0+(1\alpha)\,\lambda\,\mathrm{R}\}-\{-32.3+0.5-0.7+0.4+(1\beta)\,\lambda\,\mathrm{R}\}=62.0+(1\alpha)\,\lambda\,\mathrm{R}-(1\beta)\,\lambda\,\mathrm{R}=168.2^{*23}$$

The corresponding observed value is obtained by, $\{[M]^{20}_{D}(\mathrm{W})$ of α-D-fucose$\}$ minus $\{[M]^{20}_{D}(\mathrm{W})$ of β-D-fucose$\}$. Then, if $[M]^{20}_{D}(\mathrm{W})$ of β-D-fucose, now unknown, is x,

*13 cf. *17 in this article.
*14 Ref. Eq. 32 in *32 in the previous paper 1.
*15 Ref. "Theoretical Formulae" in the previous paper 7.
7) S. Yamana, This Bulletin, **30**, 203 (1957).
*16 Eq. 12 in the previous paper 1.
*17 By using Hudson's data of β-L-arabinose (ref. *3),

$$\{(4\alpha)-(4\beta)\}\,\lambda\,\{(1\alpha)+(2\alpha)+(3\beta)+\mathrm{R}\}=-162.8 \quad (2)^*$$
$$\{(4\alpha)\,\mathrm{X}\,(\mathrm{CH_3})^{5\beta}-(4\beta)\,\mathrm{X}\,(\mathrm{CH_3})^{5\beta}\}\zeta_{OH}\zeta_{CH_3}(n^2+2/3)=32.1 \quad (3)^*$$
$$\zeta_{OH}\zeta_{CH_3}=0.6671\ (3/n^2+2) \quad (4)^*$$
$$\zeta_{CH_3}=0.4228\ (3/n^2+2)^{1/2} \quad (5)^*$$

*18 It is apparent here that $\zeta_{OH}>\zeta_{CH_2OH}>\zeta_{CH_3}$ (ref. Eq. 20 in the previous paper 1). This fact coincides with the assumption that the magnitude of ζ-coefficient depends mostly upon the degree of change of $\alpha_i\beta_i$ of an unit group by solvation (ref. *19 in the previous paper 1). In other words, the magnitude of ζ indicates roughly the degree of solvation of an unit group. Moreover it is interesting that, when Hudson's data of L-arabinoses are used, $\zeta_{OH}\zeta_{CH_3}$ (this is 0.6671 $(3/n^2+2)$) is nearly equal to $\zeta^2_{CH_2OH}$ (this is 0.6276 $(3/n^2+2)$). (ref. *17 in this article and *43 in the previous paper 1).
*19 Concerning the procedure of making the table of $[\mu]^{20}_{D\mathrm{obs}}$, refer to Eq. 3 in the previous paper 1. The values of ζ_{OH} and ζ_{CH_3} which are used for Table III, are given in *44 in the previous paper 1 and *31 in this article.
*20 Ref. *3 in the previous paper 1.
*21 It can be said that $\{(1\alpha)-(1\beta)\}\,\lambda\,\{\cdots\cdots\}$ is a formula of $[\mu]^{20}_{D\mathrm{obs}}$ of An. Diff. (cf. *12).
*22 The values in Table II are used.
*23 Eq. 13 in the previous paper 1 is used here.
*24 cf. *30.

the observed value of An. Diff. of D-fucose is $(251.0-x)$. This value should be equal to the above calculated $[\mu]^{20}_{D\,obs}$. Then $251.0-x=168.2$ hence $x=82.8$*24

By using the same method, $[M]^{20}_{D}(W)$ of β-D-isorhamnose, now unknown, is calculated as -46.6*24.

Discussion on the Results

In the previous paper[4], the author presumed the internal conformation of C^6—O bond in D-mannose molecule in aqueous solution by a new method, devised by the author, and the obtained result satisfied the conditions which were required from the viewpoint of the atomic distances in the molecule of D-mannose. By the calculation in reversing the order of this method, it becomes possible to find another method*25 of presuming the unknown $[M]^{20}_{D}(W)$, as below; according to the previous paper 1, the internal conformation of C^6—O bond in D-galactose in aqueous solution seems to be mostly of *gauche* II type. Then, the unit groups which can couple with $(OH)^1$ dynamically in this sugar are $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, $(CH_2OH)^{5\beta\cdot g\mathrm{II}}$ and Ring*26. Therefore, $[\mu]^{20}_{D\,obs}$ of An. Diff. of D-galactose is given by,

$$\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)+(3\beta)+(4\beta)+(5\beta.g\mathrm{II})+\mathrm{R}\}^{*21}=\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)+(3\beta)+(4\beta)+\mathrm{R}\}+\{(1\alpha)-(1\beta)\}\lambda(5\beta.g\mathrm{II})\equiv G$$

Whereas, $[\mu]^{20}_{D\,obs}$ of An. Diff. of D-fucose has already been given by,

$$\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)+(3\beta)+(4\beta)+(\mathrm{CH_3})^{5\beta}+\mathrm{R}\}=\{(1\alpha)-(1\beta)\}\lambda\{(2\alpha)+(3\beta)+(4\beta)+\mathrm{R}\}+\{(1\alpha)-(1\beta)\}\lambda(\mathrm{CH_3})^{5\beta}\equiv H$$

Then, the difference between these two $[\mu]^{20}_{D\,obs}$, (G and H), is as follows;

$$G-H=\{(1\alpha)-(1\beta)\}\lambda(5\beta.g\mathrm{II})-\{(1\alpha)-(1\beta)\}\lambda(\mathrm{CH_3})^{5\beta}=\{(1\alpha)\lambda(5\beta.g\mathrm{II})-(1\beta)\lambda(5\beta.g\mathrm{II})\}-\{(1\alpha)\lambda(\mathrm{CH_3})^{5\beta}-(1\beta)\lambda(\mathrm{CH_3})^{5\beta}\}\simeq(1\alpha)\lambda(\mathrm{OH})^{6\cdot g\mathrm{II}}\text{*}^{27}-(1\beta)\lambda(\mathrm{OH})^{6\cdot g\mathrm{II}}=7.3\text{*}^{28}$$

*25 In this method, ζ_{CH_3} is needless.

*26 Ref. Table I in the previous paper 1.

*27 $(OH)^{6\cdot g\mathrm{II}}$ means OH group which combines with C^6-atom in *gauche* II conformation (i.e. OH group in $(CH_2OH)^{5\beta\cdot g\mathrm{II}}$), and so on.

The corresponding observed value is given by, $(271.5-95.1)$*26 $-(251.0-x)$*28 $=x-74.6$.

As these two values should be equal to each other,

$$7.3=x-74.6 \quad \therefore \quad x=81.9$$

This is the presumed value of $[M]^{20}_{D}(W)$ of β-D-fucose, by the new method without using ζ_{CH_3}. By using the same method*29, $[M]^{20}_{D}(W)$ of β-D-isorhamnose can be calculated to be -43.4*24. These presumed values are not exactly but approximately consistent with those, calculated by using ζ_{CH_3} in "Method Proposed" of this article, (82.8 and -46.6), respectively.

Comparing these calculated values by two different methods with each other,

*28 Concerning the process of this simplification, refer to "Method Proposed" in the previous paper 4. And here, the optical center of OH group is located at the center of mass of C—(OH) bond.

*29 {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-mannose} minus {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-rhamnose} $\simeq(1\alpha)\lambda(\mathrm{OH})^{6\cdot ma}-(1\beta)\lambda(\mathrm{OH})^{6\cdot ma}$*28; {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-glucose} minus {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-isorhamnose} $\simeq(1\alpha)\lambda(\mathrm{OH})^{6\cdot ma}-(1\beta)\lambda(\mathrm{OH})^{6\cdot ma}$*28 $\therefore$ {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-mannose} minus {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-rhamnose} = {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-glucose} minus {$[\mu]^{20}_{D\,obs}$ of An. Diff. of D-isorhamnose}. This equation can be rewritten by using the corresponding observed values, as below; {$[M]^{20}_{D}(W)$ of An. Diff. of D-mannose} minus {$[M]^{20}_{D}(W)$ of An. Diff. of D-rhamnose} = {$[M]^{20}_{D}(W)$ of An. Diff. of D-glucose} minus {$[M]^{20}_{D}(W)$ of An. Diff. of D-isorhamnose}; $\{52.8-(-30.6)\}-\{15.7-(-63.0)\}=\{202.1-33.7\}-\{120.3-x\}$*8,*24,*26 or $x=-43.4$.

*30 When using Hudson's data of L-arabinoses (ref. *17 in this article), $[\mu]^{20}_{D\,obs}$ of An. Diff. of D-rhamnose is 78.6 (Eq. 13* in *35 of the previous paper 1 is used here). (This is just equal to its corresponding observed value, 78.7). The presumed values of $[M]^{20}_{D}(W)$, in this case, are as below; β-D-fucose (86.2) (This is somewhat greater than that, calculated in "Method Proposed" and "Discussion on the Results" in this article.); β-D-isorhamnose (-43.2).

*31 For comparison, the calculated values by supposing that the optical centers of OH and CH_3 groups are located at their respective O and C atoms, are given here (cf. *44 in the previous paper 1),

	Isbell and Pigman's data of L-arabinoses	Hudson's data of L-arabinoses
ζ_{CH_3}	0.2880 $(3/n^2+2)^{1/2}$	0.6206 $(3/n^2+2)^{1/2}$
$[M]^{20}_{D}(W)$ of β-D-fucose	83.6	87.8
$[M]^{20}_{D}(W)$ of β-D-isorhamnose	-46.1	-41.9

$[M]_D^{20}$(W) of β-D-fucose, and β-D-isorhamnose are presumed to be about 81.9～82.8 and −46.6～−43.4 respectively*[31].

Summary

It was concluded by PM-method that the principle of optical superposition of Kirkwood's idea exists in methyl pentoses, and two $[M]_D^{20}$(W), formerly unknown, were presumed.

The author wishes to express his deepest thanks to Professor S. Tanaka (Kyoto University) for his valuable discussion and encouragement throughout the course of this study.

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The Synthesis of Carvone from α-Terpinyl Acetate

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(Received February 22, 1958)

Up to the present, the synthesis of *l*-carvone from *d*-limonene has been attained through the intermediates of *d*-limonene nitrosochloride and *l*-carvoxime[1,2]. In these cases the conversion of limonene into carvone resulted in relatively high yields (35% and 56～60%, respectively), but it was necessary to use toxic nitrosylchloride gas. Recently, two alterative methods[3] of the conversion of *d*-limonene into *l*-carvone have been reported. The first involves conversion of limonene monoxide into limonene glycol, oxidation of the glycol to a keto alcohol with *tert*-butyl chromate, and dehydration of the keto alcohol to *l*-carvone. In the second, the oxide is first converted into limonene glycol diacetate, which is in turn pyrolyzed to carveol acetate, saponified to carveol, and then oxidized to carvone. The overall yields of *l*-carvone from *d*-limonene in these cases do not exceed 9.2% and 7%, respectively.

Oppenauer and Oberrauch[4] previously found that *tert*-butyl chromate, described by Wienhaus and Treibs[5], is useful as an oxidant, and that *tert*-butyl chromate dissolved in a non-polar solvent with addition of a small amount of an organic acid oxidizes the methylene group adjacent to a double bond to the ketonic group without attacking the double bond.

The oxidation of terpene compounds with *tert*-butyl chromate has been investigated in this laboratory, and it has been reported that the oxidation of α-pinene[6] gives mainly verbenone and a little verbenyl acetate, and the oxidation of carvomenthene[7] produces carvotanacetone. It has been also described by Dupont et al.[8] that, on oxidation with *tert*-butyl chromate, carvomenthene yields carvotanacetone and piperitone, both α- and β-pinenes give verbenone only, and camphene remains unchanged. Thus it is evident that when a terpene hydrocarbon containing an isolated double bond is treated with *tert*-butyl chromate, the methylene group in the α-position to an ethylenic linkage in the ring is oxidized to a ketonic group.

Oxidation of α-terpineol with tert-butyl chromate[9]. The author considered that, if the methylene group adjacent to the ethylenic linkage of α-terpineol (I_a) was oxidized to a ketonic group with *tert*-butyl chromate as in the cases of terpene hydrocarbons and if 8-hydroxycarvotanacetone (II_a) was thus obtained in a high

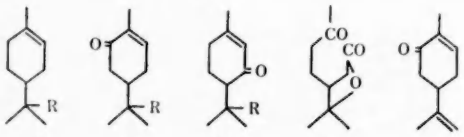
1) C. Bordenca, F. K. Allison and P. H. Dirstine, *Ind. Eng. Chem.*, **43**, 1196 (1951).
2) E. E. Royals and S. E. Horne, Jr., *J. Am. Chem. Soc.*, **73**, 5856 (1951).
3) S. M. Linder and F. P. Greenspan, *J. Org. Chem.*, **22**, 949 (1957).
4) R. V. Oppenauer and H. Oberrauch, *Anales Asoc. Quim. Argentina*, **37**, 246 (1949).
5) H. Wienhaus and W. Treibs, *Ber.*, **56**, 1648 (1923).
6) T. Matsuura and K. Fujita, *J. Sci. Hiroshima Univ.*, **A16**, 173 (1952).
7) K. Fujita and T. Matsuura, ibid., **A18**, 455 (1955).
8) G. Dupont, R. Dulou and O. Mondou, *Bull. soc. chim. France*, **1953**, 60.
9) T. Matsuura and T. Suga, *J. Chem. Soc. Japan, Pure Chem. Soc. (Nippon Kagaku Zassi)*, **78**, 1117 (1957).

TABLE I
CONDITIONS AND RESULTS IN OXIDATION OF *dl*-α-TERPINEOL

Expt.	Conditions			Reaction Products**		
	Sample/Chromic acid (mole ratio)	Temp. (°C)	Time*	8-Hydroxy-carvotan-acetone (%)	8-Hydroxy-piperitone (%)	Homoterpenyl methyl ketone (%)
1	I:5	50	36 hr., then 4 days at R.T.	8	5	22
2	1:2.5	35	36 hr., then 12 hr., at R.T.	I5	7	20
3	1:2.5	20	10 days at R.T.	14	7	18

* R.T.: Room temperature.
** Yields represent wt.% for α-terpineol used.

yield, it would be possible to convert the latter into carvone by dehydration to form an isopropenyl group from the hydroxy-isopropyl group. Then, an attempt was first made to study the action of *tert*-butyl chromate on *dl*-α-terpineol. A benzene solution of *tert*-butyl chromate containing glacial acetic acid and acetic anhydride was used as an oxidizing agent, and the oxidation was carried out in a current of carbon dioxide under three different conditions as shown in Table I. From the results (Table I) it was found that the reaction products consisted of 8-hydroxycarvotanacetone (II_a), 8-hydroxy-piperitone (III_a), a new compound, and



(I) (II) (III) (IV) (V)

a, R=OH
b, R=OAc

homoterpenyl methyl ketone (IV), but in all cases unchanged α-terpineol was recovered in amounts ranging from 32% to 44%.

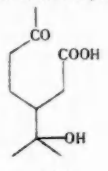
Considerable amounts of homoterpenyl methyl ketone were produced from α-terpineol by oxidative fission of the double bond in the ring. Such cleavage occurred scarcely ever or only a little in the oxidation of α-pinene, carvomenthene and limonene (to be described later). It was difficult to suppress the cleavage of the ethylenic bond even by using milder conditions, viz., a small amount of the oxidant at a low temperature (e.g., Expt. 3).

Oxidation of α-terpinyl acetate with tert-butyl chromate[10]. Accordingly it is of interest to attempt an oxidation of *dl*-α-terpinyl acetate (I_b) to see whether, by acetylating the hydroxyl group of α-terpineol, it is possible to suppress the cleavage reaction of the ethylenic linkage in the ring*.

A benzene solution of *tert*-butyl chromate (three moles of chromic anhydride to one mole of α-terpinyl acetate) containing glacial acetic acid and acetic anhydride was used as in the case of α-terpineol. Treatment of α-terpinyl acetate with this oxidant at room temperature (the average temperature was 20°C) for fifteen days in a current of carbon dioxide led to the formation of 8-acetoxycarvotanacetone (II_b) (the yield was 23% to α-terpinyl acetate), which had not yet been described, and homoterpenyl methyl ketone (15%), but in this case no product resulting from the oxidation of the methylene group in the $C_{(3)}$ position of α-terpinyl acetate was detected. The oxidation of a large amount of α-terpinyl acetate, however, gave a small amount (ca. 3%) of a new compound, 8-acetoxypiperitone (III_b), in which the methylene group in the $C_{(3)}$ position was changed into a ketonic group, while the yields of 8-acetoxycarvotanacetone and homoterpenyl methyl ketone were

10) T. Matsuura, T. Suga and K. Suga, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1122 (1957).

* It is interpreted by J. L. Simonsen ("The Terpenes", University Press, Cambridge, 1947, Vol. 1, p. 259) that on oxidation of α-terpineol, homoterpenyl methyl ketone is formed by loss of water from a γ-hydroxyacid (VI).



(VI)

26% and 10%, respectively. A respectable amount of α-terpinyl acetate (26% and 43%, respectively) was recovered unchanged.

Thus it was made quite clear that, on action of *tert*-butyl chromate on α-terpinyl acetate, the oxidation of the methylene group in the $C_{(6)}$ position in the ring to a ketonic group (to give 8-acetoxycarvotanacetone) proceeds prominently, while both the oxidation of the $C_{(3)}$ position (to 8-acetoxypiperitone) and the cleavage of the double bond (to homoterpenyl methyl ketone) are restrained.

Dehydroacetoxylation of 8-acetoxycarvotanacetone[11]. There have been a great deal of works showing that the pyrolysis of esters is an excellent method for the introduction of the unsaturated linkage, and it has frequently been used for the syntheses of olefins. Bailley et al.[12] have recently shown that the vapor phase pyrolysis of acetates of secondary and tertiary alcohols proceeds selectively with the formation of the least alkylated olefin, and the direction of elimination is always such that the hydrogen is abstracted in the order: primary>secondary >tertiary. It has also been reported by Aratani and Matsuura[13] that the pyrolysis of terpin diacetate produced β-terpinyl acetate in 57% yield.

It is of interest, therefore, to study the pyrolysis of 8-acetoxycarvotanacetone (II_b) to produce carvone (V) by the elimination of acetic acid.

The pyrolysis was carried out by the distillation through a Vigreux column under an atmospheric pressure in an air-bath, the temperature of which was raised gradually from the room temperature to 340°C during the operation. Acetic acid was liberated in an amount of 92% of the theoretical and the pyrolysate which distilled out was 91% of the starting material. The pyrolysate freed from acetic acid gave a neutral oil (66%), which contained 72% (or 59% of the theoretical amount to the starting material) of the desired ketone, *dl*-carvone, and the undesired substances, carvacrol (7%) and piperitenone (13%). It was sure that piperitenone was formed through the dehydroacetoxylation of 8-acetoxypiperitone which existed as a contaminate in 8-acetoxycarvotanacetone. A small amount (ca. 7%) of 8-acetoxycarvotanacetone was recovered.

Thus, it has been established that when 8-acetoxycarvotanacetone is pyrolyzed in the liquid phase, the dehydroacetoxylation takes place in the direction of a primary hydrogen atom to form an isopropenyl group and gives a relatively high yield of *dl*-carvone.

Selection of the conditions in the oxidation of α-terpinyl acetate. As mentioned above, the pyrolysis of 8-acetoxycarvotanacetone proceeds in a highly selective manner to give the prominent yield of carvone, but the conversion of α-terpinyl acetate into 8-acetoxycarvotanacetone is unsatisfactory in respect of the yield under the employed circumstances.

An extensive study was then made in order to develop a satisfactory procedure for the conversion of α-terpinyl acetate into 8-acetoxycarvotanacetone and to accumulate, in addition, fundamental data for the *tert*-butyl chromate oxidation. The effects of the solvent, (acetic acid), and the reaction temperature, and the catalytic action of benzoyl peroxide, on the yield of the reaction products from oxidation of α-terpinyl acetate, particularly the desired α,β-unsaturated ketone, were studied.

The relative yields of crude 8-acetoxycarvotanacetone in the reaction mixtures were determined by measuring the absorption at the maximum 235 mμ, specific to the α,β-unsaturated ketone, and the yields were estimated by weighing the desired ketone isolated by fractional distillation.

To examine the effect of the solvent on the yield, *n*-hexane, carbon tetrachloride, and benzene, were compared under the identical conditions (Expt. 1, 2 and 3 in Table II), and benzene was found the best. Therefore, benzene was henceforward used as the solvent for *tert*-butyl chromate.

Next, the influence of aeration was examined. The experiments showed that the yield of the α,β-unsaturated ketone in the acidic oxidation (Expt. 3 and 4) was greater in the current of air than in the current of carbon dioxide, but such was not the case in the neutral oxidation (Expt. 5 and 6). The results were similar irrespective of the amounts of the oxidant (Expt. 7 and 8) and of the acid (Expt. 9 and 10). The increase in the yield, however, seems not to be concerned with a simple autoxidation, because α-terpinyl acetate was fairly indifferent to air in

11) T. Suga and T. Matsuura, ibid., **78**, 1089 (1957).
12) W. J. Bailey, et al., *J. Am. Chem. Soc.*, **77**, 75, 357 (1955).
13) T. Aratani and T. Matsuura, *J. Sci. Hiroshima Univ.*, **A20**, 191 (1957).

the same medium and under the same conditions as in the acidic oxidation (Expt. 11), infrared absorption (Fig. 1) showing that α-terpinyl acetate was not changed by air.

Further, in the acidic oxidation in the current of either carbon dioxide or air, the yield of α,β-unsaturated ketone increased with the addition of increasing quantities of acetic acid. However, the increase in the acid made difficult the separation of the benzene layer from the aqueous layer in the treatment of the reaction mixture with water.

The effect of the temperature on the yield of the products was studies with the results as follows. In the oxidation with the acidic oxidant in the air-stream, elevation of the temperature from 30°C to 50°C* brought a significant increase in the yield of the α,β-unsaturated ketone even when the amount of acetic acid was small (Expt. 12). The yield of the ketone was somewhat greater when more acid was used (Expt. 13), reaching 45% to α-terpinyl acetate used.

Thus it was established that the desired α,β-unsaturated ketone is produced in 45% yield to α-terpinyl acetate when the oxidation using the fixed quantity of the benzene solution of *tert*-butyl chromate (the mole ratio of α-terpinyl acetate to chromic anhydride is 1 : 2.7) is carried out with the addition of ca. 9% acetic acid at 50°C for one hundred hours in the current of air.

Then, in the acidic oxidation in the current of carbon dioxide, the effect of benzoyl peroxide, which has been frequently used as an initiator of radical reactions, was examined (Expt. 14 and 15). The acidic oxidation in the presence of benzoyl peroxide was carried out at 55°C, since it has been reported[14,15] that the catalytic ability of benzoyl peroxide increases with the elevation of the temperature, and results in an increase in the yield of the α,β-unsaturated ketone, compared with the oxidation in the absence of the peroxide.

Though not yet examined, a larger excess of the oxidant with benzoyl peroxide and air may increase more remarkably the yield of the desired ketone.

It was thus established that the conversion of *dl*-α-terpinyl acetate into *dl*-carvone through 8-acetoxycarvotanacetone is effected by means of the combined procedure of the *tert*-butyl chromate oxidation and the pyrolysis, giving an overall yield of 28 mole%.

In conclusion, it may be added that Fujita[16] of this laboratory treated *d*-limonene with a benzene solution of *tert*-butyl chromate containing acetic acid and acetic anhydride at 50°C for a period of thirty-six hours and obtained chiefly *dl*-carvone in a yield of 20% to limonene along with *d*-isopiperitenone (13%) and piperitenone (3%).

Experimental

Oxidation of *dl*-α-Terpineol—Expt. 2 (Table I) is described below in details. Expt. 1 and 3 followed in the wake of Expt. 2.

dl-α-Terpineol[17], b.p.$_2$ 79~80°C, n_D^{25} 1.4814, d_4^{25} 0.9310, was prepared by refluxing terpin hydrate with 0.5% aqueous solution of oxalic acid for 5 hr. and by rectifying the crude product.

tert-Butyl chromate[4] was prepared by adding 163 g. of chromic anhydride in small portions to 325 g. of *tert*-butyl alcohol with ice-cooling, diluting the resultant with 1000 g. of benzene, drying the resulted benzene solution over anhydrous sodium sulfate, and concentrating it to 75 vol.% in vacuo. To the solution were added 55 g. of glacial acetic acid and 75 g. of acetic anhydride just prior to the oxidation.

Oxidation and treatment of reaction products.—To 100 g. of α-terpineol in 150 g. of dry benzene was added dropwise the above oxidant in a period of 4 hr. with agitation at 35°C, and then the mixture was maintained at the same temperature for 32 hr. with stirring in an atmosphere of carbon dioxide, and left to stand at the room temperature for 12 hr. When the reaction was over, the whole reaction mixture was treated with 500 cc. of water and 290 g. of hydrated oxalic acid with vigorous stirring. The mixture was separated into two layers and the aqueous solution was repeatedly extracted with benzene. The combined benzene solution was treated with aqueous alkali and with water successively and dried. After removal of the solvent, 78.5 g. of a neutral oil was obtained (Product A). The alkaline solution was repeatedly extracted with ether and chloroform in succession. From the both extracts 4.5 g. of a brown viscous oil was obtained (Product B).

Identification of products.—Distillation of Product A at 7 mmHg gave the following four fractions: (A) b.p.$_7$ 82~86°C, n_D^{25} 1.4775~1.4792, d_4^{25} 0.9445~0.9516, yield 43.9 g.; (B) b.p.$_7$ 111~121°C, n_D^{25} 1.4832~1.4850, d_4^{25} 1.0182~1.0202, yield 6.6 g.;

* It is described[4] that *tert*-butyl chromate explodes when heated above 60°C.

14) S. Kamenskaya and S. Medvedev, *Acta Physicochim.*, **13**, 565 (1940); *Chem. Abst.*, **35**, 2400 (1941).

15) M. F. R. Mulcahy and I. C. Watt, *J. Chem. Soc.*, **1954**, 2971.

16) K. Fujita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1112 (1957).

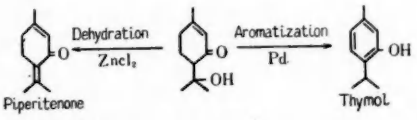
17) K. Ono and Z. Taketa, *Reports of Saisei Shôno Co.*, **1**, 11 (1924).

(C) b.p.$_7$ 146~151°C, n_D^{25} 1.4914, d_4^{25} 1.0325, yield 14.9 g.; (D) b.p.$_7$ 166~170°C, yield 16.2 g.

(1) 8-Hydroxypiperitone (III_a). Ultraviolet absorption spectrum of fraction B gave λ_{max}^{alc}: 235mμ (strong), which corresponded to the *K*-band of the α,β-unsaturated ketone[18], and 276mμ (very weak). The chromatogram on Kirchner's chromatostrip[19], developed with 45 vol.% ethyl acetate in *n*-hexane and sprayed with 2,4-dinitrophenylhydrazine—hydrochloric acid, gave two spots. One, R_f value=0.20, was large and distinct, while the other, R_f value=0.73, was small and faint. Accordingly, the weak band at 276mμ seemed to be attributable to the impurity which gave the spot, R_f value=0.73. The heating of 3.3 g. of fraction B with 0.4 g. of palladium charcoal[20] (palladium: 30%) at 240~245°C for 9 hr. in the current of carbon dioxide gave 2.1 g. of thymol. This fact was established by the following procedures: (a) Ultraviolet absorption spectrum of the oil obtained exhibited the same λ_{max}^{alc} 277mμ (ε: 1870) as λ_{max}^{alc} 277mμ (ε: 2400) of thymol. (b) On heating with phthalic anhydride in presence of conc. sulfuric acid, thymolphthalein was obtained. (c) An alkaline solution of monochloroacetic acid[21] gave thymoxyacetic acid, m.p. and mixed m.p. 149~149.5°C.

Next, a mixture of 0.89 g. of fraction B, 0.90 g. of xylene and 0.09 g. of anhydrous zinc chloride was heated at 140°C for 0.5 hr. with agitation. This treatment gave 0.57 g. of piperitenone. This fact was confirmed by the following procedures: (a) Ultraviolet absorption spectrum exhibited λ_{max}^{alc} 242mμ (ε: 4760) and 276mμ (ε: 3180) identical with the *K*-band of the cross conjugated dienone chromophore in piperitenone[22]. (b) The chromatogram on chromatostrip did not give a spot of R_f value 0.20 corresponding to the original ketone but gave a spot of R_f value 0.73 corresponding to piperitenone. (c) A warm solution of 2,4-dinitrophenylhydrazine in alcoholic hydrochloric acid gave an isomeric mixture of piperitenone 2,4-dinitrophenylhydrazone. The separation by chromatography on silica—plaster of Paris (4:1) with benzene—petroleum ether (1:1) gave two isomers*, m.p. 152~153°C (67%) and m.p. 183.5~184°C (33%), of the 2,4-dinitrophenylhydrazone. Each showed no depression on admixture with the known specimens.

The results are schematically summarized as follows:



Thus, it was evident that fraction B consisted of 8-hydroxypiperitone.

(2) 8-Hydroxycarvotanacetone. (II_a) The chromatostrip—chromatogram of fraction C by the same method as above gave a single spot, R_f value=0.33. Ultraviolet absorption spectrum exhibited λ_{max}^{alc} 235mμ.

Treatment of a part of this fraction with palladium charcoal gave carvacrol, which was identified as the phenylurethane, m.p. and mixed m.p. 134.8~135°C.

Fraction C gave a semicarbazone, m.p. 175~176°C, and an oxime, m.p. 133~134°C. These were identified as the derivatives of 8-hydroxycarvotanacetone by mixing with known samples. By the treatment with a warm solution of 2,4-dinitrophenylhydrazine in alcoholic hydrochloric acid, 2,4-dinitrophenylhydrazone, m.p. 201~201.5°C (*Anal.* Found: N, 16.23. Calcd. for $C_{16}H_{20}O_5N_4$: N, 16.08%), was obtained.

Thus, it was established that fraction C consisted of 8-hydroxycarvotanacetone.

Ultraviolet absorption spectra of the derivatives: semicarbazone, λ_{max}^{alc} 264mμ (ε: 24000); oxime, λ_{max}^{alc} 234mμ (ε: 16300); 2,4-dinitrophenylhydrazone, λ_{max}^{alc} (the principal band) 378mμ (ε: 26650).

2,4-Dinitrophenylhydrazone of 8-hydroxycarvotanacetone, and ultraviolet absorption spectra of the ketone and its derivatives, have not yet been described in the literatures.

(3) Homoterpenyl methyl ketone (IV). Fraction D solidified. The crystalline product had m.p. 62~63°C. Its semicarbazone had m.p. 205~206°C. Product B (described above), after being distilled (b.p.$_4$ 154~160°C), also gave a semicarbazone, m.p. 204.5~205°C. These were identified as homoterpenyl methyl ketone and its semicarbazone by mixing with the genuine specimens. From fraction D, 2,4-dinitrophenylhydrazone, m.p. 164~164.5°C (*Anal.* Found: N, 15.53. Calcd. for $C_{16}H_{20}O_6N_4$: N, 15.38%) was quantitatively prepared.

(4) Unchanged α-terpineol (I_a). Fraction A gave *dl*-α-terpinyl phenylurethane, m.p. and mixed m.p. 112~113°C, and nitrosochloride, m.p. and mixed m.p. 112~113°C.

Further, from the recovered benzene solution, a small amount of acetone was isolated as the semicarbazone, m.p. and mixed m.p. 187~188°C.

Oxidation of *dl*-α-Terpinyl Acetate—*dl*-α-*Terpinyl acetate*, b.p.$_{15}$ 112~113.5°C, n_D^{25} 1.4638, d_4^{25} 0.9563, ester value 286.4 (calcd. for $C_{12}H_{20}O_2$: 285.9), was prepared by refluxing *dl*-α-terpineol with acetic anhydride and anhydrous sodium acetate in xylene and by rectifying the product.

I. Identification of the Reaction Products.—To 90 g. of α-terpinyl acetate was added dropwise a benzene solution of *tert*-butyl chromate, which was prepared from 255 g. of *tert*-butyl alcohol, 138 g. of chromic anhydride, 560 g. of benzene,

18) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, **1941**, 815; ibid., **1943**, 565.

19) J. G. Kirchner, J. M. Miller and G. J. Keller, *Anal. Chem.*, **23**, 420 (1951); J. M. Miller and J. G. Kirchner, ibid., **25**, 1107 (1953).

* Y. R. Naves[22] isolated the three isomers, m. p. 132~133°C, m. p. 152~153° and m. p. 183.5~184°C. We could also isolate these three isomers in another part of the experiments (described later).

20) R. P. Linstead, K. O. A. Michaelis and S. L. S. Thomas, *J. Chem. Soc.*, **1940**, 1139.

21) F. Koelsch, *J. Am. Chem. Soc.*, **53**, 304 (1931).

22) Y. R. Naves, *Bull. soc. chim. France*, **1951**, 370.

100 g. of acetic acid and 100 g. of acetic anhyride, in a period of 6.5 hr. with stirring and cooling in ice, and then the mixture was maintained at the room temperature (20°C averaged) for 15 days with occasional agitation. Treated in the same way as in the case of α-terpineol, the benzene solution gave 59.5 g. of a neutral oily product and the alkaline aqueous solution gave 10.0 g. of a viscous oil (b.p.$_{12}$ 180~184°C).

Distillation of the neutral oily product at 7mmHg gave the following three fractions: (A) b.p.$_7$ 93~98°C, n_D^{25} 1.4592, d_4^{25} 0.9718, yield 23.1 g.; (B) b.p.$_7$ 139~142°C, n_D^{25} 1.4706, d_4^{25} 1.0498, yield 17.9 g.; (C) b.p.$_7$ 145~160°C, n_D^{25} 1.4737, d_4^{25} 1.0495, yield 6.2 g.

(1) 8-Acetoxycarvotanacetone (II_b). Ester value of fraction B was 263.6 (calcd. for $C_{12}H_{18}O_3$: 266.3). The λ_{max}^{alc} 235mμ in ultraviolet spectrum and the wave number of 1672 cm.$^{-1}$ (liquid film) in infrared spectrum indicated the presence of a ketonic group conjugated with a double bond. In the infrared spectrum, wave numbers 1729 cm.$^{-1}$ and 1246 cm.$^{-1}$, characteristic of acetate, were also observed. The saponified product gave 8-hydroxycarvotanacetone semicarbazone and oxime.

These results established that fraction B consisted of 8-acetoxycarvotanacetone.

The derivatives of 8-acetoxycarvotanacetone and their ultraviolet absorption spectra were as follows:

Semicarbazone, m.p. 191.5~192°C, λ_{max}^{alc} 264mμ (ε: 23710).

Anal. Found: C, 58.23; H, 7.91; N, 15.85. Calcd. for $C_{13}H_{21}O_3N_3$: C, 58.41; H, 7.92; N, 15.72%.

Oxime, m.p. 107.2~107.5°C, λ_{max}^{alc} 233mμ (ε: 15870).

Anal. Found: C, 64.16; H, 8.36; N, 6.51. Calcd. for $C_{12}H_{19}O_3N$: C, 63.98; H, 8.50; N, 6.22%.

2,4-Dinitrophenylhydrazone, m.p. 217.8~218°C, λ_{max}^{alc} (a principal band) 376mμ (ε: 27580).

Anal. Found: N, 14.64. Calcd. for $C_{18}H_{22}O_6N_4$: N, 14.35%.

(2) Homoterpenyl methyl ketone (IV). Fraction C (6.2 g.) was saponified with alkali and extracted with ether. From the ethereal solution 3.0 g. of 8-hydroxycarvotanacetone was isolated as the semicarbazone. The residual alkaline solution, after being acidified with dilute sulfuric acid and extracted with chloroform, gave 3.2 g. of homoterpenyl methyl ketone. The viscous oil (10.0 g.), b.p.$_{12}$ 180~184°C, from alkaline aqueous solution (vide ante) was also homoterpenyl methyl ketone.

(3) Unchanged α-terpinyl acetate (I_b). Ester value of fraction A was 283.2 (calcd. for $C_{12}H_{20}O_2$: 285.9). The saponified product gave *dl*-α-terpinyl phenylurethane and nitrosochloride.

(4) 8-Acetoxypiperitone (III_b). When 280 g. of α-terpinyl acetate was oxidized with *tert*-butyl chromate, prepared from 852 g. of *tert*-butyl alcohol, 426 g. of chromic anhydride, 3360 g. of benzene, 420 g. of acetic acid and 320 g. of acetic anhydride, at 50°C for 36 hr. and then at the room temperature for 3 days, 249 g. of the neutral oxidation product was obtained.

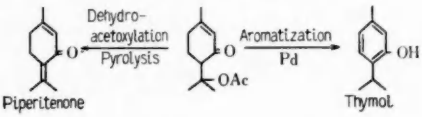
The product gave unchanged α-terpinyl acetate (43% to α-terpinyl acetate used), 8-acetoxycarvotanacetone (26%), homoterpenyl methyl ketone (10%) and a fraction of b.p.$_{3.5}$ 100~120°C, n_D^{25} 1.4670, d_4^{25} 1.0100, yield 7.3 g. (ca. 3%), which was the intermediate fraction between α-terpinyl acetate and 8-acetoxycarvotanacetone.

Ultraviolet absorption spectrum of this fraction exhibited λ_{max}^{alc} 235mμ (very strong) and 277mμ (very weak). In the chromatogram on chromatostrip, developed with 30 vol. % ethyl acetate in *n*-hexane and sprayed with 2,4-dinitrophenylhydrazine—hydrochloric acid, the major portion (λ_{mex}^{alc} 235mμ) gave a large spot, R_f value=0.38 and the weak 277mμ band seemed to be attributable to an impurity which gave a faint spot, R_f value=0.62.

2,4-Dinitrophenylhydrazone, after being chromatographed on silica—plaster of Paris (4:1) with benzene—petroleum ether (1:1) and recrystallized from ethyl acetate, had m.p. 166~166.5°C and λ_{max}^{alc} 378mμ (ε: 30650) in the ultraviolet absorption spectrum. This absorption band and the λ_{mx}^{alc} 235mμ of the original ketone support that the ketonic group is conjugated with a double bond. The analysis of the hydrazone, C, 55.36; H, 5.74; N, 14.42%, agreed with the calculated values for $C_{18}H_{22}O_6N_4$ (8-acetoxypiperitone 2,4-dinitrophenylhydrazone): C, 55.38; H, 5.68; N, 14.35%.

Treatment of the fraction with palladium charcoal in the same manner as in the case of 8-hydroxypiperitone gave thymol and acetic acid (identified by paper-chromatography of the hydroxamic acid prepared[23]). The fraction (3.5 g.) was gently heated from 200°C to 300°C in an air-bath for 1.5 hr., and a distillate, b.p. 110~231°C, was collected. The distillate gave 0.91 g. (91% of the theoretical) of acetic acid and 1.2 g. of piperitenone. The identity of the piperitenone was established by the same way as in the case of 8-hydroxypiperitone.

The establishment of 8-acetoxypiperitone was schematically summarized as follows:



Acetone was also isolated as the semicarbazone from the recovered benzene solution in a very small amount.

II. Selection of the Conditions of the Oxidation.—Oxidation was carried out in a flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a gas inlet tube opening directly beneath the stirrer. The flask was held in a constant-temperature bath which could be regulated to ±1°C. Air, dried with conc. sulfuric

23) Y. Inoue and M. Noda, *J. Agr. Chem. Soc. Japan, (Nippon Nôgei-Kagaku Kaishi)* **23**, 294 (1950); **24**, 291 (1951).

TABLE II
THE CONDITIONS OF OXIDATION AND THE YIELDS OF CRUDE 8-ACETOXYCARVOTANACETONE

Expt.	Sample	Conditions of oxidation							Product
	α-Terpinyl acetate (g.)	Terpinyl acetate/Chromic acid (mole ratio)	Sol-* vent	Acetic acid (g.)	Acetic anhydride (g.)	Gas** passed	Temp. (°C)	Time (hr.)	Crude*** 8-acetoxy-carvotan-acetone (%)
1	50	1:2.7	H	20	50	C	30	100	10.9
2	50	1:2.7	C	20	50	C	30	100	11.7
3	50	1:2.7	B	20	50	C	30	100	15.6
4	50	1:2.7	B	20	50	A	30	100	23.0
5	50	1:2.7	B	—	—	C	30	100	7.4
6	50	1:2.7	B	—	—	A	30	100	7.5
7	50	1:0.4	B	2.4	4.0	C	30	60	8.0
8	50	1:0.4	B	2.4	4.0	A	30	60	12.0
9	50	1:2.7	B	200	100	C	30	100	26.3
10	50	1:2.7	B	200	100	A	30	100	40.0
11	50	—	B	20	50	A	30	100	—
12	50	1:2.7	B	20	50	A	50	100	41.2
13	50	1:2.7	B	100	50	A	50	100	44.8
14	50	1:2.7	B	100	50	C	55	100	43.0
15****	50	1:2.7	B	100	50	C	55	100	53.2

* H: *n*-Hexane. C: Carbon tetrachloride. B: Benzene.
** C: Carbon dioxide. A: Air.
*** Yields represent wt.% for α-terpinyl acetate used.
**** The oxidant contains benzoyl peroxide.

acid and calcium chloride, was passed in at 350 cc. per min.

In all experiments listed in Table II except Expt. 7 and 8, *tert*-butyl chromate was prepared from 138 g. of *tert*-butyl alcohol, 69 g. of chromic anhydride and 1060 cc. of the solvent in the same way as above. In Expt. 7 and 8, 20.4 g. of *tert*-butyl alcohol, 10.2 g. of chromic anhydride and 114 cc. of benzene were used. Acetic acid and acetic anhyride were added as shown in Table II. In Expt. 15 benzoyl peroxide, which corresponded to 2 mole % for α-terpinyl acetate, was further added to the acidic oxidant just prior to the oxidation.

In all cases, the oxidant was added at a time to 50 g. of α-terpinyl acetate dissolved in 57 cc. of the solvent. When oxidation was over, the same treatment of the oxidation mixture as above gave a neutral reaction mixture. The relative yield of α,β-unsaturated ketone in each reaction mixture was determined by measuring ultraviolet absorption spectrum at 235mμ (in ethyl alcohol). Then, the reaction mixture was fractionally distilled under the reduced pressure of carbon dioxide. The fractions were separated into the unchanged and the changed parts by the chromatostrip color test and the yield of crude 8-acetoxycarvotanacetone was determined.

The conditions employed and the results obtained are summarized in Table II.

In Fig. 1 the infrared spectra (liquid film) of the reaction mixture in Expt. 11 and of *dl*-α-terpinyl acetate used were compared in the 2000~750 cm.$^{-1}$ range. Agreement between these spectra showed that in Expt. 11, *dl*-α-terpinyl acetate was not at all attacked by air.

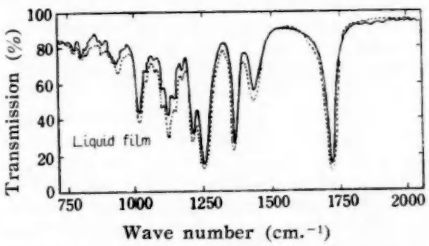


Fig. 1. Infrared spectra of the reaction mixture in Expt. 11 and of *dl*-α-terpinyl acetate used.
——: the reaction mixture in Expt. 11.
·····: *dl*-α-terpinyl acetate used.

In Expt. 15 (the oxidation catalyzed by benzoyl peroxide) the same reaction products were also obtained as in Expts. 1~14.

Dehydroacetoxylation of 8-Acetoxycarvotanacetone—*8-Acetoxycarvotanacetone*, b.p.$_2$ 129~131°C, n_D^{25} 1.4820, d_4^{25} 1.0434, ester value 269.5 (calcd. for $C_{12}H_{18}O_3$: 266.8), was prepared by oxidation of *dl*-α-terpinyl acetate with *tert*-butyl chromate. The chromatogram on chromatostrip indicated that this ketone was contaminated by a small amount of 8-acetoxypiperitone.

Dehydroacetoxylation. — 8-Acetoxycarvotanace-

tone (35.7 g.) was distilled under an atmospheric pressure in a distilling flask equipped with a Vigreux column, the temperature of the air-bath being raised slowly to 340°C in a period of 4 hr. Dehydroacetoxylation took place actively at bath temperature 220~280°C (the reaction mixture 200~240°C). A pyrolysate (32.3 g., 91% to 8-acetoxycarvotanacetone), b.p. 114~245.5°C, distilled out leaving 2.8 g. (8%) of a polymer. Acid value of the pyrolysate was 271.0, corresponding to 9.4 g. (92% of the theoretical) of acetic acid.

Treatment and identification of the pyrolysate.— The pyrolysate was shaken with a dilute sodium bicarbonate solution to remove acetic acid, which was identified as *p*-acetotoluide. The solution of the neutral oil in petroleum ether was quickly shaken with a 5% sodium hydroxide solution. The alkaline solution was repeatedly extracted with ether. The ethereal solution gave 1.1 g. of carvacrol, which was characterized as the phenylurethane, m.p. and mixed m.p. 134.5~135.5°C. The petroleum ether solution gave 21.2 g. of a neutral oil.

Distillation of the oil at 5 mmHg gave the following three fractions: (A) b.p.$_5$ 85~90°C, n_D^{25} 1.4978~1.4985, d_4^{25} 0.9569~0.9571, yield 14.9 g.; (B) b.p.$_5$ 90~122°C, n_D^{25} 1.5200~1.5232, d_4^{25} 0.9746~0.9829, yield 5.6 g.; (C) b.p.$_5$ 122~126°C, yield 0.6 g.

(1) *dl*-Carvone (V). Ultraviolet absorption spectrum of fraction A exhibited λ_{max}^{alc} 235mμ identical with that of carvone[24]. The chromatogram on chromatostrip, developed with 30 vol. % ethyl acetate in *n*-hexane and sprayed with 2,4-dinitrophenylhydrazine — hydrochloric acid, gave a single spot. This fraction yielded *dl*-carvone semicarbazone, m.p. and mixed m.p. 155~156°C, *dl*-carvoxime, m.p. and mixed m.p. 92~92.5°C, and 2,4-dinitrophenylhydrazone, m.p. 187~187.2°C[25] (*Anal.* Found: N, 17.03. Calcd. for $C_{16}H_{18}O_4N_4$: N, 16.96%). These showed that this fraction consisted of *dl*-carvone only.

(2) Piperitenone. Ultraviolet absorption spectrum of fraction B showed λ_{max}^{alc} 243mμ and 277mμ, and the chromatogram on the chromatostrip developed as above gave three spots which possessed R_f value 0.75, 0.62 and 0.51, respectively. Then, 1.0 g. of fraction B was separated into these fractions by the elution-chromatography on silica (20 g.) with *n*-hexane—ether (3:2).

The fraction, yield 36%, which gave a spot of R_f value 0.75, consisted of *dl*-carvone (77%) and carvacrol (23%).

The fraction, yield 59%, which gave a spot of R_f value 0.62, consisted of piperitenone. This was established as follows: (a) Ultraviolet absorption spectrum exhibited λ_{max}^{alc} 243mμ (ε: 9930) and 277mμ (ε: 7250) characteristic of piperitenone[22]. (b) Treatment of 0.20 g. of this fraction with palladium charcoal gave 0.18 g. of thymol. (c) Ozonolysis of the fraction in ethyl acetate—acetic acid gave levulinic acid (semicarbazone, m.p. and mixed m.p. 183.2~184°C) and acetone (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 123~125°C). (d) The separation of 2,4-dinitrophenylhydrazone by chromatography on silica—plaster of Paris with benzene—petroleum ether and recrystallization gave three isomers, (i) m.p. 151~152°C, λ_{max}^{alc} 387mμ (ε: 29780), (*Anal.* Found: C, 58.30; H, 5.96; N, 16.94%). (ii) m.p. 132~133°C, λ_{max}^{alc} 388mμ (ε: 29700). (iii) m. p. 183.8~184.5°C, λ_{max}^{alc} 389mμ (ε: 27520). (*Anal.* Found: C, 58.23; H, 5.66; N, 17.39. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96%). These were identical with the three isomers of piperitenone 2,4-dinitrophenylhydrazone reported by Naves[22], respectively.

The fraction, yield 5%, which gave a spot of R_f value 0.51, yielded 2,4-dinitrophenylhydrazone in reddish violet needles, m.p. 171~171.5°C, λ_{max}^{alc} 392mμ. The fraction was so small that it was not investigated further.

(3) Unchanged 8-acetoxycarvotanacetone. 2,4-Dinitrophenylhydrazone of fraction C, chromatographed on alumina with benzene, melted at 215~216°C. It was identified as 8-acetoxycarvotanacetone 2,4-dinitrophenylhydrazone.

Summary

(1) Oxidation of *dl*-α-terpineol with *tert*-butyl chromate yielded 8-hydroxypiperitone, which has not previously been described, 8-hydroxycarvotanacetone and homoterpenyl methyl ketone. In this case the oxidative fission of the double bond in the ring took place to a remarkable extent.

(2) Oxidation of *dl*-α-terpinyl acetate with *tert*-butyl chromate gave 8-acetoxypiperitone, 8-acetoxycarvotanacetone (neither have previously been described) and homoterpenyl methyl ketone. In this oxidation the cleavage of the ethylenic linkage was suppressed, and the yield of 8-acetoxycarvotanacetone was relatively good.

Moreover, the effects of the solvent, acetic acid, benzoyl peroxide, air, and the reaction temperature, on the yield of 8-acetoxycarvotanacetone were investigated.

(3) 8-Acetoxycarvotanacetone was converted into *dl*-carvone when acetic acid was eliminated by pyrolysis.

(4) The synthesis of carvone from α-terpinyl acetate was attained through the intermediate of 8-acetoxycarvotanacetone. The overall yield of carvone from α-terpinyl acetate was 28 mole%.

The author wishes to express his hearty gratitude to Professor Tamon Matsuura for his guidance and encouragement, to

24) R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, **1938**, 1408.

25) A. Kergomard [*Ann. chim.* (*Paris*), **8**, 193 (1953)] has reported m.p. of *dl*-carvone 2,4-dinitrophenylhydrazone to be 185~186°C.

Assistant Professor Syûichi Hayashi for his advice, and to Mr. Tadami Sakoda, Miss Miyoko Sakai and Mrs. Kiyoko Suga who assisted in a part of the experiment. This research was aided by a grant from the Ministry of Education.

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The Mechanical Behavior of Swollen Polymethyl Acrylate Gels. I. The Determination of Polymer-Solvent Interaction Parameter μ by the Mechanical Measurement

By Kazuyoshi OGINO

(Received January 20, 1958)

When a slightly cross-linked linear chain polymer is in contact with a solvent, it absorbs the solvent and expands to a limited volume, attaining the so-called swollen gel state. In this case, the interaction forces between the polymer and the solvent are considered to be one of the important factors which determine the degree of swelling of this system. A parameter which is called the polymer-solvent interaction patameter μ is employed to express the power of solvation. Mullin[1] showed that this parameter could be determined mechanically by the measurement of initial stress-strain relations using a gel of vulcanized natural rubber swollen in an organic solvent.

In this paper, the author determined this parameter μ of slightly cross-linked polymethyl acrylate gels swollen in several organic solvents, following the same method reported by Mullin.

Theory

The force f required to strain a gel to an extension ratio λ is given by[2]

$$f=2A_0(\lambda-\lambda^{-2})v_r^{-1/3}(\partial W/\partial I_1+\lambda^{-1}\partial W/\partial I_2) \tag{1}$$

where A_0 is the unstrained area of cross section, v_r the volume fraction of polymer at swelling equilibrium, W the free energy of deformation per unit volume, called as the stored energy function, and I_1 and I_2 are strain invariants which are defined as follows;

$$I_1=\lambda_1^2+\lambda_2^2+\lambda_3^2$$
$$I_2=\lambda_1^{-2}+\lambda_2^{-2}+\lambda_3^{-2}$$

where λ_1, λ_2 and λ_3 are the principal extension ratios.

This relation can also be expressed as follows[1]

$$f=2A_0(\lambda-\lambda^{-2})v_r^{-1/3}(C_1+\lambda^{-1}C_2) \tag{2}$$

In this relation, C_1 and C_2 are constants, and are obtained experimentally. Since the value of C_2 decreases to zero at a high degree of swelling ($v_r \leqq 0.25$), the equation 1 or 2 is reduced to the form predicted by the kinetic theory, if

$$C_1(\text{swollen})=\frac{1}{2}\cdot\rho\cdot R\cdot T\cdot M_c^{-1} \tag{3}$$

where ρ is the density of pure solvent, and M_c a parameter, which can be assumed as the average molecular weight between junction points.

On the other hand, at swelling equilibrium with solvent, the following equation is obtained from statistical consideration[3],

$$\ln(1-v_r)+v_r+\mu v_r^2=-\rho V_0 v_r^{1/3}/M_c \tag{4}$$

Or, from equation 3

$$-\ln(1-v_r)-v_r-\mu v_r^2=2V_0C_1v_r^{1/3}/RT \tag{5}$$

In practice, the value of C_1 for a swollen gel can be obtained either by direct measurements of a high degree of swelling or by plotting the results of the simple extension measurement as

1) L. Mullin, *J. Polym. Sci.*, **19**, 225 (1956).
2) S. M. Gumbrell, L. Mullin and R. S. Rivlin, *Trans. Faraday Soc.*, **49**, 1495 (1953).
3) P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943); M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 1712 (1942).

$f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} and extrapolating the curve to $\lambda^{-1}=0$.

With the value of C_1 thus obtained, the parameter μ can be determined by the equation 5.

Experimental

Sample — Commercial methyl acrylate was purified by shaking with aqueous alkaline solution, and was redistilled under reduced pressure. Diallyl adipate which was used as cross-linking agent was synthesized by esterification of allyl alcohol with adipic acid in the presence of *p*-toluene sulfonic acid as catalyst, and purified by fractional distillation under reduced pressure.

α-α'-azodi-*iso*-butyronitrile, used as initiator, was prepared according to Thiele and Heuser[4], and was recrystalized from ether.

About 8 cc. of methyl acrylate monomer which contains one drop (about 3 mg.) of the cross-linking agent and about 30 mg. of the initiator was polymerized in bulk in a sealed glass tube. The polymer rod was then cut into several pieces, about 1 cm. in length, and immersed into the solvent to be tested.

Organic solvents used in this experiment are chloroform, benzene, toluene and carbon tetrachloride. They were purified in the usual way.

Apparatus.—The apparatus used in this experiment is shown in Fig. 1[5,6]*.

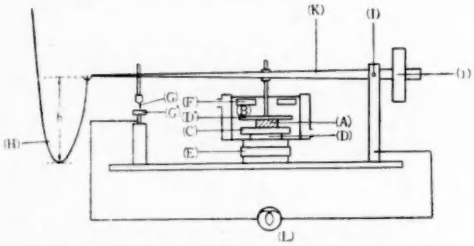

Fig. 1. The apparatus used in this experiment.
A: Specimen. B: Solvent. C: Iris of microscope. D: Brass block. D': Pressure plate. E: Screw gauge. F: Desiccating agent. G and G': Contacts. H: Chain. I: Fulcrum. J: Balancing weight. K: Beam.

Specimen A in the swelling equilibrium with a solvent B was placed between a flat brass block D and a pressure plate D', and was strained to a definite extent by rotating the screw E which was graduated to 0.01 mm., and the stress was measured by the chain H with the known linear density.

Force f in equation 2 at each strain can be calculated by the following equation

$$f=(bdhg)/a$$

where d is the linear density of the chain, h the vertical component of the chain length suspended from the beam, b the distance from the fulcrum to the chain, a the distance from the fulcrum to the center of the pressure plate and g the acceleration of gravity. In this experiment, $b/a\approx 4.3$, and d was 0.80 or 0.39 g/cm.

The temperature of the sample was controlled by circulation of water from a water bath kept at 25±0.5°C, and was read directly by a thermometer inserted in the solvent.

Results and Discussion

When W_b and W_a are the weights of the polymer before and after swelling, ρ_1 and ρ_2 are the densities of the solvent and of the polymer, respectively, the volume fraction v_r of the polymer after swelling can be given by the following equation[7];

$$v_r=\frac{1}{1+\frac{\rho_2}{\rho_1}\left(\frac{W_a}{W_b}\right)-\frac{\rho_2}{\rho_1}}$$

The results are shown in Table I. The solvent, in which a gel has a small value

TABLE I
THE VALUES OF VOLUME FRACTION OF POLYMER, v_r, AND μ AT 25°C.

Solvent	v_r	$1/v_r$	$\mu_{25°C}$
Chloroform	0.035_5	28.2	0.49
Benzene	0.065_9	15.2	0.51
Toluene	0.192_5	5.2	0.54
Carbon Tetrachloride	0.501_0	2.0	0.69

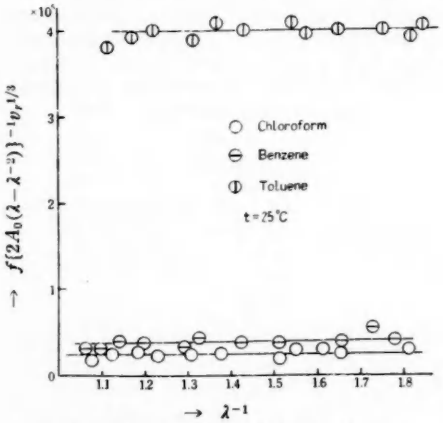

Fig. 2. The plot of $f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} at 25°C.

* This apparatus has been designed for the measurement of stress relaxation.

4) J. Thiele and K. Heuser, *Ann.*, **290** (1896).
5) S. L. Dart and E. Guth, *J. Appl. Phys.*, **17**, 314 (1946).
6) H. Fujita, K. Ninomiya and T. Homma, This Bulletin, **25**, 374 (1952).
7) P. Doty and H. S. Zable, *J. Polym. Sci.*, **1**, 90 (1946).

of v_r, may be considered approximately to be a good solvent, because polymer-solvent contacts are attained sufficiently in it. From this table, we can assume that the solvent becomes poorer in the order of chloroform, benzene, toleuene and carbon tetrachloride.

An example for the plot of $f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} is shown in Fig. 2. There is a good linear relationship between these two quantities. Extrapolation of the curve to $\lambda^{-1}=0$ gives C_1. The value of μ can be determined with the use of these values of C_1 and v_r. The results are shown in Table I. These values are about 0.50 except for carbon tetrachloride, and decrease in the order, toluene>benzene>chloroform. We can say that chloroform is the best solvent for polymethyl acrylate in these four solvents, and carbon tetrachloride is the poorest solvent.

The gradient of the lines in Fig. 2 is identified with C_2, and this can be regarded as zero from this figure. The value of C_2 can be considered to show the degree of the restriction to the possible configuration of the molecular chain, and therefore those solvents, in which the interaction forces between long chain molecules can be considered to be fairly loosen, are good.

Doty and Zable[7] showed that $\mu=0.55$ is the border-line between poor solvent and non-solvent. Huggins[8] showed that $\mu=0.50$ is the border-line between poor and good solvent. Further, in the case of gel, μ depends upon the concentration of cross-linking agent[9]. On the other hand, the different values of μ for the same polymer-solvent system are reported by the different workers, even if the values are determined mechanically by the same method[2].

In this experiment, from the considerations on the values of v_r, μ or C_2, the author has assumed that chloroform, benzene and toluene are good solvents and carbon tetrachloride is a poor solvent. The values of μ obtained at 31, 25 and 15°C seem to show, also, that benzene is a good solvent**.

From the accuracy in the determination of μ, especially from its temperature dependency, the results obtained in this experiment are not enough to be discussed in detail. There are also some questions concerning the effect of cross-linking agent as mentioned above. However, the values of μ obtained here seem to be not so unreasonable compared with the other workers' results.

The author is indebted to Professor H. Akamatu and Assistant Professor T. Nakagawa for their interest in and support of this experiment.

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8) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).
9) R. F. Boyer and R. S. Spencer, *J. Polym. Sci.*, **3**, 97 (1948).
** These values are; $\mu_{31}=0.51_6$; $\mu_{25}=0.51_3$; $\mu_{15}=0.50_9$.

The Mechanical Behavior of Swollen Polymethyl Acrylate Gels. II. The Stress Relaxation in Organic Solvents

By Kazuyoshi OGINO

(Received February 4, 1958)

In the previous paper[1] the interaction parameter μ between polymer and solvent has been determined for slightly cross-linked polymethyl acrylate gels in equilibrium with several organic solvents, from their initial stress-strain relations. Although these gels respond purely elastically to a rapid deformation, it is observed that the stress relaxes with time under a constant deformation. The stress relaxation and its dependency upon the degree of swelling of these gels are investigated in the present paper.

The stress-strain behavior of a viscoelastic body may be expressed by the Maxwell equation, or by generalizing the Maxwell theory in consideration of a distribution of relaxation times.

If the distribution of relaxation times is continuous, the rate of strain, ds/dt, is expressed as,

$$\frac{ds}{dt} = \frac{1}{E(\tau)} \cdot \frac{df(\tau,t)}{dt} + \frac{1}{\tau \cdot E(\tau)} \cdot f(\tau,t)$$

where $f(\tau,t)$ and $E(\tau)$ are the distribution functions of the stress and the elastic modulus respectively. Total stress is expressed as,

$$f(t) = \int_0^\infty f(\tau,t)d\tau.$$

Then, at a constant strain s_0, the decay of stress with time can be expressed as follows:

$$f(t) = \int_0^\infty s_0 \cdot E(\tau) \cdot \exp \cdot (-t/\tau) \cdot d\tau = s_0 E(t) \qquad (1)$$

where $E(t)$ is the relaxation elastic modulus, which can be determined by the experiment. $E(\tau)$, which is the distribution function of elastic modulus, is a fundamental measure of the mechanical behavior of a substance. Several methods have been proposed to obtain this function approximately from the experimental curves[2].

As a first approximation we can replace the function $\exp.(-t/\tau)$ in equation 1 by step function $K(t,\tau)$, which is defined as follows:

$$K(\tau,t) = \begin{cases} 1 \cdots\cdots t<\tau \\ 0 \cdots\cdots t>\tau \end{cases}$$

Then equation 1 turns out to be

$$E(t) = \int_t^\infty E(\tau) \cdot d\tau$$

then,

$$E(\tau) = -dE(t)/dt$$

Using the latter relation, we can obtain the distribution function of elastic modulus among the various relaxation times experimentally from the negative slope of the observed relaxation curve.

On the other hand, Tobolsky et al. found that[3] the shape of the relaxation curve for a given polymer is the same at different temperatures, when plotted as reduced stress* against logarithmic time, but a change in temperature essentially shifts the position of the curve along the logarithmic time scale.

Experimental

Sample. — Cross-linked polymethyl acrylate used in this experiment is the same as described in the previous paper[1]. Samples are brought to the swelling equilibrium with chloroform, benzene, toluene, carbon tetrachloride and methanol.

Apparatus. — The specimen is vertically compressed to a given height, and the stress which corresponds to the strain is recorded continuously by means of a chainomatic balance (the same one as was used in the previous work[1]) which is equipped with an automatically balancing system. This is shown in Fig. 1. The apparatus is the same as originally used by Guth[4] for the measurement of stress relaxation of cork, and recently improved by Fujita et al.[5].

1) K. Ogino, This Bulletin, **31**, 577 (1958).
2) H. Fujita, *Busseiron Kenkyu*, **63**, 48 (1953), (*in Japanese*)

* The stress is arbitrarily reduced to 25°C. The reduced stress g_{25} is calculated by multiplying the actual experimental stress value, f, by $298/T$, where T is absolute temperature.

3) A. V. Tobolsky et al., *J. Polym. Sci.*, **3**, 669 (1948).
4) S. L. Dart and E. Guth, *J. Apply Phys.*, **17**, 314 (1946).
5) H. Fujita, K. Ninomiya and T. Homma, This Bulletin, **25**, 271 (1952).

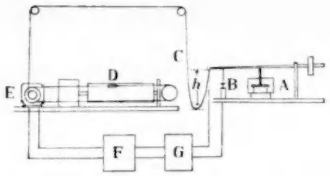

Fig. 1. The apparatus for the measurement of stress relaxation.
(A): Specimen (B): Contact
(C): Chain (D): Pencil for recording
(E): Balancing motor (F): Relay
(G): Amplifier circuit

In Fig. 1, (A) is the specimen at a given constant strain, and the stress is measured by the suspended length of a chain (C), which is controlled by the reversible motor (E) through the relay (F) and the amplifier circuit (G).

The reduced stress g_{25} at t°C can be expressed as follows

$$g_{25} = \frac{h \cdot d \cdot G \cdot n}{A_0} \cdot \frac{298}{t+273} \text{ dyne/cm}^2$$

where, h the vertical component of the chain length from the arm, d the linear density of the chain, n the magnification of the arm, that is the ratio of the distances to the hook and to the pressure plate from the fulcrum, A_0 the cross-sectional area of the sample, t the temperature of the sample and G is the acceleration of gravity. In this apparatus, n is about 4.3. The experimental curves of reduced stress against logarithmic time scale obtained by this method are shown in Fig. 2.

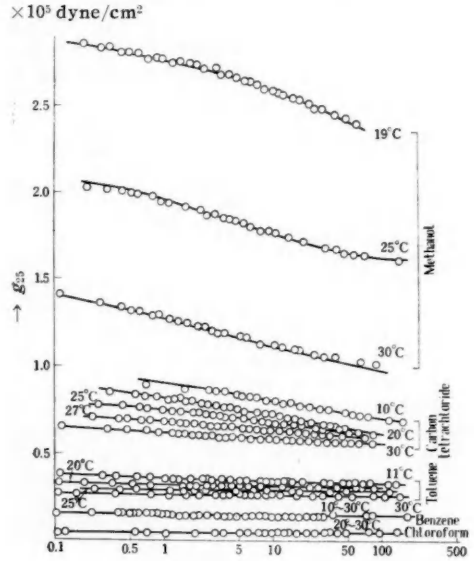

Fig. 2. The curves of reduced stress g_{25} against logarithmic time.

Results and Discussion

It is obvious from Fig. 2 that the smaller degree of swelling corresponds to the larger magnitude of stress, and to the larger degree of stress relaxation. For the good solvents, such as benzene or chloroform, relaxation curves at different temperatures expressed in reduced stress nearly overlap with each other. The slight dependency upon temperature means the small activation energy in relaxation.

Stress relaxation corresponds primarily to the breakage of some sort of linkage, such as secondary bonds or entanglement which are formed in the gel structures. As weak linkages may exist hardly at all in the well-swollen gels, only some strong linkages remain unbroken. As the weak linkages which are present at lower temperatures would be broken at higher temperatures, the degree of relaxation at higher temperatures is less remarkable than at lower temperatures. The greater temperature dependency, i. e., the greater activation energy, is expected for a poor solvent than for a good solvent. (Tobolsky has calculated this apparent activation energy for relaxation process[3,6]. But in this work, its calculation was not carried out, considering the large error involved in the data of the initial stress.) When the curves in Fig. 2 are superposed upon each other by sliding along the logarithmic time scale, master curves as shown in Fig. 3 are obtained. The slope of the master curve is large for the small degree of swelling, and for the high degree

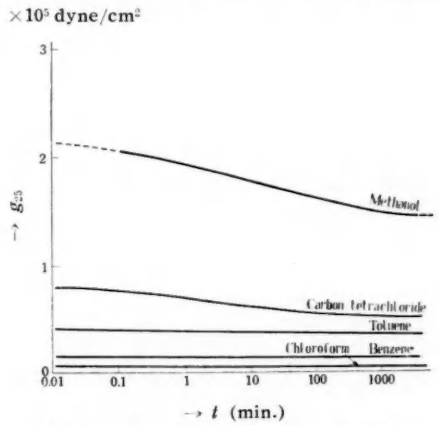

Fig. 3. The master curve of gels for each solvent.

6) G. M. Brown and A. V. Tobolsky, *J. Polym. Sci.*, **6**, 165 (1951).

of swelling, a constant slope over the wide range of the time scale is observed. This means that the height of distribution function $E(\tau)$ becomes higher, while its width is restricted, when the degree of swelling is small.

For the actual relaxation phenomena, the continuous distribution of relaxation times must be taken into account as mentioned above. However, how these phenomena can be expressed by the spring-dashpot model is now considered, applying the four-element system as shown in Fig. 4. To determine the magnitude of each parameter in this system, from actual relaxation data, the following method has been proposed[7].

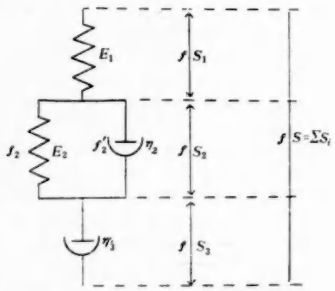

Fig. 4. The four-element model.

In the model shown in Fig. 4, the total strain $s=\sum_j s_j$, and f is the reactant stress.

Thus the following equations are obtained:

$$f/s_1=E_1$$

$$f_2/s_2=E_2 \quad : \quad f'_2/\dot{s}_2=\eta_2 \quad : \quad f_2+f'_2=f$$

$$f/\dot{s}_3=\eta_3$$

From these relations, we obtain at a constant strain,

$$\ddot{f}+\left\{E_1\left(\frac{1}{\eta_2}+\frac{1}{\eta_3}\right)+\frac{E_2}{\eta_2}\right\}\dot{f}+\frac{E_1E_2}{\eta_2\eta_3}\cdot f=0 \qquad (1)$$

The solution of equation 1 can be expessed as follows

$$f=Ae^{-\alpha t}+Be^{-\beta t} \qquad (2)$$

where,

$$\begin{cases} 2\alpha=\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right] \\ \qquad -\sqrt{\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right]^2-4\dfrac{E_1E_2}{\eta_2\eta_3}} \\ 2\beta=\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right] \\ \qquad +\sqrt{\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right]^2-4\dfrac{E_1E_2}{\eta_2\eta_3}} \end{cases} \qquad (2')$$

If a rapid strain $s=s_0$ was given at $t=0$, from equation 2,

$$\begin{cases} A=\dfrac{-\beta f_{t=0}-\dot{f}_{t=0}}{\alpha-\beta} \\ B=f_{t=0}-A \end{cases} \qquad (3)$$

and,

$$\begin{cases} E_1\cdot s_0=f_{t=0} \\ \dfrac{\dot{f}_{t=0}}{E_1}=-\dfrac{f_{t=0}}{\eta_2}-\dfrac{f_{t=0}}{\eta_3} \quad \text{or} \quad \dfrac{1}{\eta_2}+\dfrac{1}{\eta_3}=-\dfrac{s_0\cdot\dot{f}_{t=0}}{f^2_{t=0}} \end{cases} \qquad (3')$$

From these general relations, we can determine the values of four parameters.

For simplicity, we calculate for the case when $\alpha \ll \beta$. For the large value of $t=t_l$, we can neglect the second term in equation 2 and,

$$\alpha=-\dot{f}_{t=t_l}/f_{t=t_l} \qquad (4)$$

$$A=\frac{f_{t=t_l}}{e^{(\dot{f}_{t=tl}/f_{t=tl})\cdot t_l}} \qquad (5)$$

From equation 3, 4 and 5, we obtain

$$B=f_{t=0}-\frac{f_{t=t_l}}{e^{(\dot{f}_{t=tl}/f_{t=tl})\cdot t_l}} \qquad (6)$$

$$\beta=(-\dot{f}_{t=0}-\alpha A)/B \qquad (7)$$

and from equation 2'

$$\alpha+\beta=(E_1/\eta_3+E_2/\eta_2+E_1/\eta_2) \qquad (8)$$

$$\alpha\beta=E_1E_2/\eta_2\eta_3 \qquad (9)$$

From 4—7, we obtain α, β, A and B, and with these values, from 8 and 9, we obtain two equations for parameters. Combining these equations with equation 3', we can calculate four parameters. These parameters at 25°C calculated by this method are listed in Table I.

These results show that at the small degree of swelling, or at the large value of v_r, the values of each parameter become larger. This is naturally expected from the fact that the small degree of swelling means the large concentration of the polymer substance in gel.

E_1 is the so-called instantaneous elasticity, and has a large value for the small degree of swelling. This may be due to the presence of many remaining secondary bonds besides the strong primary bonds for the small degree of swelling**. η_3 is the viscosity coefficient for the flow after the attainment of the stationary flow, and

7) T. Alfrey, "Mechanical Behavior of High Polymers", Interscience Pub., Inc., N.Y. (1948) p. 181.

** From the theory of rubber elasticity, for instance, the stress is inversely proportional to the average molecular weight, M_c, between the junction points.

TABLE I
THE VALUS OF EACH PARAMETER FOR FOUR-ELEMENT MODEL

Solvent	Parameter						
	v_r	E_1 dyne/cm².	E_2 dyne/cm².	η_2 poise	η_3 poise	η_2/E_2 sec.	η_3/E_1 sec.
Methanol	0.68	0.98×10^6	5.2×10^6	1.5×10^9	9.6×10^{11}	3.0×10^2	1.0×10^6
Carbon tetrachloride	0.50	$3.9_7\times10^5$	8.4×10^5	2.9×10^8	1.1×10^{11}	3.5×10^2	2.6×10^5
Toluene	0.19	2.0×10^5	1.6×10^6	6.5×10^7	4.2×10^{10}	4.0×10^1	2.1×10^5
Chloroform	0.036	$3.4_5\times10^4$	5.1×10^5	2.3×10^7	$8.9_7\times10^9$	4.0×10^1	2.5×10^5

has also a large value for the small degree of swelling. Such a flow may have originated from the squeezing out of solvent which is contained between networks, or from the breaking of many junction points. These inferences are consistent with the order of the degree of swelling and the value of η_3. η_2 and E_2 characterize the part which expresses the transient state from instantaneous deformation to final steady flow, which occurs in a comparatively short time after the strain is imposed ($10^1\sim10^2$ sec., expected from η_2/E_2 in Table I), and may reflect the change of the inner structures. η_2 and E_2 have always larger values as the degree of swelling is lower. Taking account of the fact that η_2 and E_2 large, it seems that the weaker bond would be broken faster after the strain is imposed, or the solvent which can be pushed out more easily from the network would be squeezed out more readily.

In chloroform or benzene, polymer swells to a large extent, so that the greater part of the gel is occupied by solvent. The appearance of this gel is very soft. The mechanical behavior of these gels can be expressed by a simple Maxwell model as shown in Fig. 5 ($\ln f/f_0$ plotted against t). The slope of this curve gives $-1/\tau$, where τ is relaxation time. The relaxation time obtained from this method is approximately in agreement with the value η_3/E_1 of the four element model.

Chain molecules in these gels are fixed

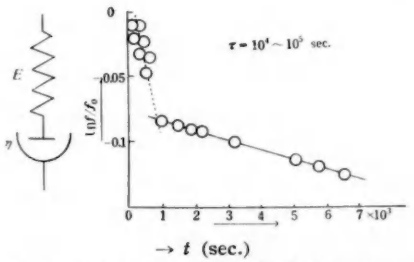

Fig 5. The curve plotted $\ln f/f_0$ against t for benzen.

at several junction points by cross-linking, and the interaction between these chains is considered to be stronger than in an ordinary polymer solution. The effect of this interaction appeared in the difference of dependency of stress relaxation upon the degree of swelling. The more detailed discussion must be expected from thermodynamic consideration of elasticity.

The author is particulary indebted to Professor H. Akamatu and Assistant Professor T. Nakagawa for their discussion and encouragement during this investigation, and to Mr. H. Arakawa, the University of Shizuoka, especially for his suggestion about the analysis by a four-element model.

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The Mechanical Behavior of Swollen Polymethyl Acrylate Gels. III. Thermoelastic Properties of Swollen Gels

By Kazuyoshi OGINO

(Received February 4, 1958)

When a gel is in equilibrium with a solvent, the degree of swelling and its mechanical properties depend upon the intermolecular interaction. This is shown in the preceding paper[1] for the phenomena of stress relaxation.

Gee investigated the effect of several kinds of solvent upon the elasticity of rubber[2], and pointed out that the elasticity observed in his experiment does not always coincide with the result expected from statistical theories proposed by Flory, or James and Guth[3].

Continuing from the preceding paper, the author has observed the temperature dependence of the elastic behavior of polymethyl acrylate gel in two kinds of solvent which have different powers for the polymer.

The external force of extension f is expressed as

$$f=(\partial G/\partial l)_T$$

when the volume dose not change during the deformation, where G is free energy and l is the length of the body.

As the entropy S is $S=-(\partial G/\partial T)_l$, one may write $(\partial S/\partial l)_T=-(\partial f/\partial T)_l$.

The thermodynamical relation can be expressed as,

$$(\partial G/\partial l)_T=(\partial H/\partial l)_T+T(\partial f/\partial T)_l$$

or

$$(\partial H/\partial l)_T=f-T(\partial f/\partial T)_l$$

where H is the enthalpy.

Using the extension ratio $\alpha=l/l_0$, where l_0 is the initial length, the following relation can be deduced.

$$(\partial G/\partial \alpha)_T=fl_0 \qquad (1)$$

$$(\partial H/\partial \alpha)_T=fl_0-Tl_0(\partial f/\partial T)_\alpha \qquad (2)$$

$$T(\partial S/\partial \alpha)_T=(\partial H/\partial \alpha)_T-(\partial G/\partial \alpha)_T \qquad (3)$$

The equation 1 gives the relation between free energy change and extension ratio α when the force under the various extensions at a constant temperature is measured for a sample which has the initial length l_0; the equation 2 gives the relation to obtain the enthalpy change from the temperature dependence of force at a constant extension ratio and the values of fl_0. From equation 3 combined with equation 1 and 2, we obtain the entropy change.

Experimental

The apparatus to observe the change in force with extension is the same one as used in the previous paper[4] (cf. Fig. 1 in the reference 4). Sample is polymethyl acrylate gel, cross-linked diallyl adipate and swollen in carbon tetrachloride and benzene; the former is a poor and the latter is a good solvent as reported in the previous papers[1,4]. The stress-strain relations observed at constant temperatures are shown in Fig. 1 or Fig. 2, where the strain means the compression and the stress is the initial stress. These curves are drawn connecting the observed points by a smooth line. Some deviations of these points from the smooth curve were observed. Gee supposed that these deviations may be due to the stress relaxation in the sample[2].

It must be noticed that the initial length l_0 itself changes with variation of temperature. To give the *same* extension ratio to the sample at different temperatures, the amount of compression for the sample must be changed corresponding to each temperature. In practice, the contact (G and G' in the Fig. 1 of the reference 4) is adjusted for each run to touch slightly, and therefore the change of stress which originated from the change of initial length, l_0, by thermal expansion is cancelled by this operation, then some definite compression which is determined from the initial length of the sample at the standard temperature (30°C) is given, and the corresponding stress is measured. It seems to be more correct to assume that the value of the strain imposed on the sample is adjusted according to the linear thermal expansion of the sample. But it has not been taken into account to perform this calibration in the present experiment, because, owing to the change in the length accompanying the temperature change, precise determination of the dimension of the sample is not possible*.

1) K. Ogino, This Bulletin, **31**, 580 (1958).
2) G. Gee, *Trans. Faraday Soc.*, **42**, 585 (1946).
3) P. J. Flory, *J. Chem. Phys.*, **11**, 521 (1943). H. M. James and E. Guth, ibid. **11**, 455 (1943).
4) K. Ogino, This Bulletin, **31**, 577 (1958).

* Physical meaning of this thermal expansion is discussed in reference 2.

The temperature dependency of the stress is determined from the values at several strains on each curve in Fig. 1 or Fig. 2. The results are shown in Fig. 3 and Fig. 4.

$(\partial f/\partial T)_\alpha$ is calculated by multiplying the slopes of each curve in Fig. 3 or Fig. 4 by the cross sectional area of the specimen. Also we obtain $(\partial G/\partial\alpha)_T$ from f and l_0 for each extension ratio at constant temperature. $(\partial H/\partial\alpha)_T$ and $T(\partial S/\partial\alpha)_T$ can be calculated from these values with equations 2 and 3. $(\partial G/\partial\alpha)_T$, $(\partial H/\partial\alpha)_T$ and $T(\partial S/\partial\alpha)_T$ per cubic centimeter can be obtained by dividing these values by the volumes of each specimen.

Results and Discussion

Fig. 5 and Fig. 6 are the curves which show the calculated values of $(\partial G/\partial\alpha)$, $(\partial H/\partial\alpha)$ and $T(\partial S/\partial\alpha)$ at 30°C in these two solvents. In practice, $T(\partial S/\partial\alpha)$ is obtained graphically from the difference between $(\partial G/\partial\alpha)$ and $(\partial H/\partial\alpha)$. Free energy change at constant temperature and pressure equals the external work, and enthalpy change at constant pressure equals the change of internal energy when no volume change occurs. Fig. 5 and Fig. 6 show the direction of the change of G, H and S when strain, or α, increases.

Carbon tetrachloride is not a good solvent for polymethyl acrylate considering the degree of swelling or other experimental results, as reported in the previous papers. In this solvent, $(\partial S/\partial\alpha)$ has a positive value for increasing of α, and so the

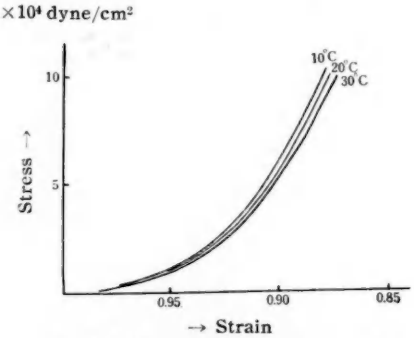

Fig. 1. The stress-strain curves for carbon tetrachloride.

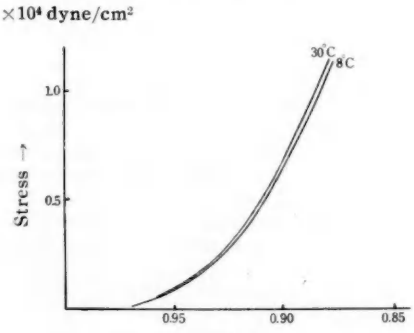

Fig. 2. The stress-strain curves for benzene.

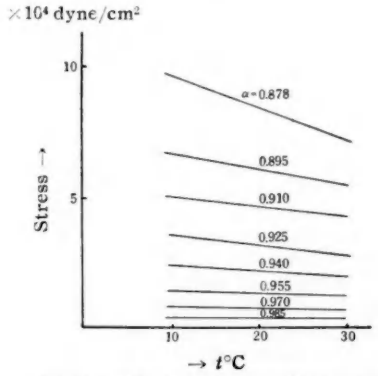

Fig. 3. The stress-temperature curves for carbon tetrachloride.

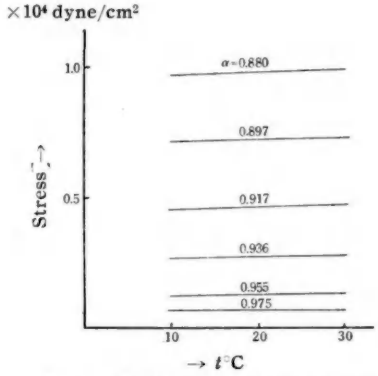

Fig. 4. The stress-temperature curves for benzene.

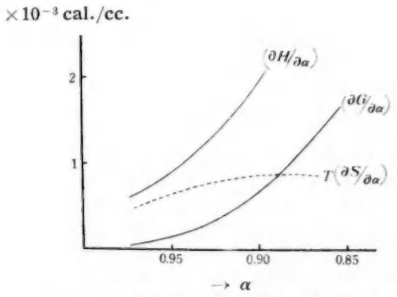

Fig. 5. Thermodynamics of compression for carbon tetrachloride.

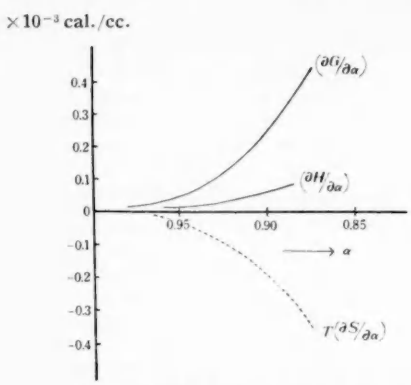

Fig. 6. Thermodynamics of compression for benzene.

magnitude of this entropy change increases with the increase of strain. Enthalpy change $(\partial H/\partial \alpha)$ is also positive, thus the change of internal energy increases with the increase of strain.

On the contrary, in benzene, polymer swells to a great extent, and in this case, with the increase of strain, the degree of the change of internal energy (positive, in this case) is not so large, and $(\partial S/\partial \alpha)$ is negative; i.e., the magnitude of entropy change decreases with increase of strain.

The increase of internal energy with extension would correspond to the fact that the external work is stored as potential energy between molecules.

In a poor solvent, like carbon tetrachloride, intermolecular interaction exists to a considerable degree, as expected from the above results. In this case, external force may loose to some extent the cohesion between molecules, and the increase of randomness of polymer molecules or the releasing of solvent molecules fixed around the polymer chains contributes to the increase of entropy of the system. These aspects seem to be acceptable from the fact that the degree of stress relaxation is more remarkable in a poor solvent, and that each parameter in four-element model is larger compared with the values obtained for a good solvent.

In the case of benzene, which is a good solvent, the decrease in entropy change is much higher than the increase in internal energy change. This may originate from the fact that the restriction for free rotation or flexion of chain molecules is removed by the high degree of swelling, and that the freedom of chain molecules is expected to decrease with the increase of strain.

Acknowledgement is made to Professor H. Akamatu and Assistant Professor T. Nakagawa for their support and advice in this experiment.

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Correction for the Intensities of Infrared Absorption Bands

By Kenji KURATANI and Atsuko MINEGISHI

(Received January 13, 1958)

The serious disadvantage of infrared absorption spectroscopy is the fact that the band shapes and the peak intensities measured in liquids or in solutions are markedly affected by the spectral slit widths of the spectrometers. Therefore it is desirable to find the method of correction of the apparent peak intensities and the band half widths to the true intensities and half widths, respectively, and to express them with the universal values. A number of authors[1-4] have discussed this problem. In the present work we have compared the methods established by these authors from the view points of the spectral slit width, the slit function, and the shape of the absorption band, and have proposed improved methods.

In the last section of this paper, the improved correction method was applied

1) D. A. Ramsay, *J. Am. Chem Soc.*, **74**, 72 (1952).
2) A. C. Hardy and F. M. Young, *J. Opt. Soc. Am.*, **39**, 265 (1949).
3) R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **9**, 133 (1957).
4) E. B. Wilson, Jr. and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946).

to the C=O stretching vibration bands of fifteen esters in carbon tetrachloride solutions, and the values of the true molecular extinction coefficient were determined. The true integrated absorption intensities per one C=O group were also obtained by the extrapolation method. These values are dispensable for the group type analysis of esters.

Correction for the Peak Intensity. Method I.—For monochromatic radiation, the well known absorption law,

$$I=I_0e^{-\alpha ct} \tag{1}$$

applies, and the true molecular extinction coefficient at the absorption maximum is described as*

$$E_{\max}=\frac{1}{ct}\log_{10}(I_0/I)_{\max} \tag{2}$$

However, in the actual spectrometer, due to the use of finite slit widths, the radiation is not monochromatic, and the energy from the exit slit of a spectrometer set at a frequency ν' may be expressed by an energy distribution function $g(\nu,\nu')$**. Accordingly when the spectrometer is set at frequency ν', the apparent intensities of the incident and transmitted radiation are described as

$$\begin{aligned} T_0&=\int I_0(\nu)g(\nu,\nu')\mathrm{d}\nu \\ T&=\int I(\nu)g(\nu,\nu')\mathrm{d}\nu \end{aligned} \tag{3}$$

and the apparent molecular extinction coefficient is given by

$$E'_{\max}=\frac{1}{ct}\log_{10}(T_0/T)_{\max} \tag{4}$$

In the actual prism spectrometer, the observed absorbances $[\log_{10}(T_0/T)=D]$ at the band peaks are markedly affected by the spectral slit widths and are very different from the true values $[\log_{10}(I_0/I)]$.

One of the well known method to correct the apparent absorbance at the band maximum for the true absorbance is proposed by Ramsay[1]. Under the following assumptions as,

i) the slit function may be represented by a triangle whose base length is equal to the twice the spectral slit width s,

ii) spectral slit width s is the sum of the term s_1 represents the contribution from the finite mechanical slit width and the term s_2 responsible for the finite resolving power of the prism, and the values of each term are evaluated by the equation given by Williams[5],

iii) the true band shape may be represented by a Lorentz curve,

$$\log_e(I/I_0)=\frac{a}{(\nu-\nu_0)^2+b^2} \tag{5}$$

Ramsay has computed the apparent band absorbance

$$\log_{10}(T_0/T)_\nu=\log_{10}\int g(\nu,\nu')\mathrm{d}\nu - \log_{10}\int g(\nu,\nu')\cdot\exp\left(\frac{-a}{(\nu-\nu_0)^2+b^2}\right)\mathrm{d}\nu \tag{6}$$

and obtained the relationships between the ratio of the true and apparent peak intensities and the ratio of the spectral slit widths to the band half widths.

However, Ramsay's assumption is not applicable to every case, and it is necessary to reexamine it. Ignoring the diffraction by a prism, the slit function for a perfectly aligned spectrometer with an equal entrance and exit slit width may be represented by a triangle as described by Ramsay. But owing to the mismatching of the curved image of the entrance slit with the exit slit curvature, the misfocusing of the collimator mirror, etc., for the spectrometer which we actually used, the slit widths of the entrance and exit slits are not equal, and therefore the shape of the slit function may be approximated more closely to trapezoid than to triangle.

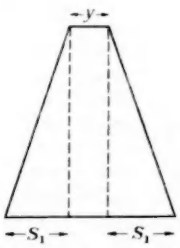

Fig. 1. Trapezoidal slit function.

Then the spectral slit width itself is rewritten as

$$s=s_1+s_2+s_3 \tag{7}$$

where s_1 and s_2 are the same as defined by Ramsay and s_3 is the term represents the contribution from opical misalignment. The details of the trapezoidal slit function illustrated in Fig. 1 are

* In this equation c is expressed moles per liter of solution and t is the cell length in cm.

** This function is defined as the slit function.

5) V. Z. Williams, *Rev. Sci. Instrumensts*, **19**, 151 (1948).

TABLE I-1

VALUES OF $\log_{10}(I_0/I)_{max}/\log_{10}(T_0/T)_{max}$ FOR THE VARIOUS VALUES OF y IN TERMS OF THE RATIO OF $s_1+y/\Delta\nu^a{}_{1/2}$*

$\log_{10}(I_0/I)_{max}/\log_{10}(T_0/T)_{max}$

$s_1+y/\Delta\nu^a{}_{1/2}$	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60
for $y'=0.000$**	1.016	1.028	1.046	1.066	1.095	1.131	1.176	1.229	1.308	1.416
for $y'=0.025$	1.013	1.025	1.041	1.061	1.088	1.124	1.167	1.220	1.295	1.396
for $y'=0.050$	1.011	1.022	1.037	1.057	1.082	1.116	1.158	1.210	1.283	1.378
for $y'=0.075$	1.011	1.019	1.033	1.052	1.076	1.108	1.150	1.200	1.270	1.364
for $y'=0.100$	1.009	1.017	1.030	1.049	1.072	1.102	1.139	1.188	1.255	1.345
for $y'=0.125$	1.009	1.016	1.028	1.045	1.066	1.095	1.133	1.180	1.245	1.330

* This Table can be applied to the values of $\log_{10}(T_0/T)_{max}$ from 0.2 to 0.4.

** The value of y' is defined as $y/\Delta\nu^t{}_{1/2}$.

TABLE I-2

VALUES OF $\Delta\nu^a{}_{1/2}/\Delta\nu^t{}_{1/2}$ FOR THE VARIOUS VALUES OF y IN TERMS OF $\log_{10}(T_0/T)_{max}=D_{max}$ AND THE RATIO OF $s_1+y/\Delta\nu^a{}_{1/2}$

$\Delta\nu^a{}_{1/2}/\Delta\nu^t{}_{1/2}$

$s_1+y/\Delta\nu^a{}_{1/2}$	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60
for $y'=0.000$										
$D_{max}=0.2$	1.021	1.038	1.060	1.091	1.131	1.180	1.242	1.320	1.422	1.550
$=0.3$	1.020	1.036	1.058	1.087	1.125	1.172	1.228	1.302	1.398	1.525
$=0.4$	1.020	1.035	1.056	1.084	1.120	1.165	1.218	1.284	1.372	1.485
for $y'=0.025$										
$D_{max}=0.2$	1.018	1.034	1.054	1.084	1.122	1.168	1.229	1.304	1.402	1.528
$=0.3$	1.018	1.032	1.053	1.081	1.117	1.162	1.216	1.287	1.380	1.502
$=0.4$	1.018	1.031	1.051	1.078	1.112	1.154	1.206	1.272	1.358	1.472
for $y'=0.050$										
$D_{max}=0.2$	1.015	1.030	1.050	1.078	1.113	1.159	1.216	1.290	1.384	1.510
$=0.3$	1.015	1.029	1.047	1.074	1.108	1.152	1.204	1.273	1.362	1.482
$=0.4$	1.015	1.027	1.045	1.071	1.103	1.144	1.195	1.258	1.343	1.452
for $y'=0.075$										
$D_{max}=0.2$	1.013	1.027	1.047	1.074	1.106	1.149	1.204	1.274	1.365	1.490
$=0.3$	1.013	1.026	1.045	1.070	1.102	1.142	1.193	1.259	1.348	1.465
$=0.4$	1.013	1.025	1.043	1.067	1.097	1.134	1.181	1.246	1.330	1.437
for $y'=0.100$										
$D_{max}=0.2$	1.012	1.024	1.042	1.066	1.098	1.138	1.191	1.262	1.348	1.472
$=0.3$	1.012	1.023	1.040	1.063	1.094	1.132	1.182	1.246	1.332	1.445
$=0.4$	1.012	1.022	1.039	1.061	1.090	1.128	1.175	1.234	1.314	1.415
for $y'=0.125$										
$D_{max}=0.2$	1.010	1.022	1.039	1.063	1.094	1.134	1.182	1.248	1.332	1.445
$=0.3$	1.010	1.021	1.037	1.059	1.088	1.124	1.172	1.233	1.314	1.425
$=0.4$	1.010	1.020	1.035	1.056	1.083	1.118	1.162	1.220	1.296	1.395

defined as follows. The length of the upper side is equal to the sum of s_2+s_3 and denoted as y, and the lower base length is equal to $2s_1+y$. This slit function is regarded as the combination of the triangular slit function whose base length is equal to twice the term which represents the contribution from the finite mechanical slit width, and the rectangular slit function whose base length is equal to the term which is responsibie for the prism diffraction and the optics misalignment.

Using the trapezoidal slit function as defined above, Eq. 6 was evaluated by numerical integration, for the various values of a, b, and the slit widths s_1 and y. For the stepwise increment of the value of y, the ratios of $\log_{10}(I_0/I)_{max}/\log_{10}(T_0/T)_{max}$ and $\Delta\nu^a{}_{1/2}/\Delta\nu'{}_{1/2}$ were represented as functions of the apparent intensities

and of the ratio $s/\Delta\nu^{a}_{1/2}$. The results are given in Table I, and the rows for $y=0$ are the same as given by Ramsay.

With this Table we can correct the observed intensities and band half widths to true ones, but it is necessary to determine the value of y experimentally, since the value of y is not known a priori. For this purpose, the absorption measurements of the same sample are made with the various mechanical slit widths, and one set of observed values for the peak intensities and band half widths are obtained. Then assuming an arbitrary y value, the spectral slit width s is determined, and the correction factor for the peak intensities observed by that slit width is found from Table I-1. Using the same y value, the similar processes are tried for the values observed with the other mechanical slit widths. If we assume an unsuitable y value, the corrected peak intensities for the various mechanical slit widths should not agree, and the similar calculations with the another y values must be repeated until we get the satisfactory agreement among the corrected intensities. The corrected peak intensities which finally agree may be considered as the true peak intensities. For the observed band half widths, the similar treatments should be made by the use of Table I-2, and the band half widths are also corrected.

This method is applied to the C=O stretching vibration bands of ethyl capronate measured in carbon tetrachloride solution, and illustrated in Table II. The corrected peak intensities show always good agreement, when we assume the value of y to be ca. 1.6 cm^{-1}. (In Table I, the correction factors are represented as the functions of $y'=y/\Delta\nu^{t}_{1/2}$ and in this case $\Delta\nu^{t}_{1/2}$ is nearly equal to 16 cm^{-1}, therefore, we get a good agreement with the value of $y'=0.1$). Therefore, when the intensity measurement in the 1700 $cm.^{-1}$ region is made with the same spectrometer under the same condition of alignment, the value of y should be always assigned to ca. 1.6 cm^{-1}*, but the value of y' should be altered according to the band half widths. In Table II, the result obtained from Ramsay's method is compared with the result of ours. The more excellent agreement among the corrected intensities is obtained with our method. The reliability of our method is also proved from the agreement between the observed resolution and the spectral slit width, and the equality between the corrected intensities and the intensities measured with a grating spectrometer under the higher resolution.

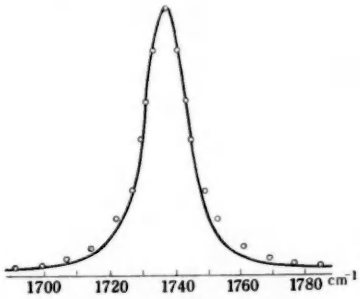

Fig. 2. Comparison between the observed and the calculated absorbance.

The aforementioned correction method is derived from the Lorentz curve approximation for the true band shape. To examine this assumption, the results of numerical integration of Eq. 6 are compared with the observed absorption curves of ethyl capronate in carbon tetrachloride solution. The results are shown in Fig. 2, where the full line represents the observed absorbance curve and the dots represent the calculated values.

The agreement between these curves is well in the central region of the bands and in the band wings, but in the middle of these regions, comparatively large differences are observed. An exponential curve, which is used by Philpotts[6] for the band shape, is also examined, but the calculated points markedly deviate from the observed curves except in the narrow central region of the bands. Therefore, for the correction of the observed peak intensities and the band half widths, it is considered to be reasonable to assume Lorentz curve for the true band shape.

Correction for the Peak Intensity. Method II.—Koana[7] and Hardy[2] showed the other correction method. For the symmetrical bands, the corrected absorbance at the band maximum (D^{0}_{max}) is represented as a first approximation by the

* The value of s_3 which represents the contribution from the misalignment of optics is nearly equal to 1.2 cm^{-1} (=1.6–0.4 cm^{-1}). This value is surprisingly large, but after the readjustment of optics, the value of s_3 was diminished to ca. 0.4 cm^{-1}.

6) A. R. Philpotts, W. Thain and P. G. Smith, *Anal. Chem.*, **23**, 268 (1951).

7) K. Koana, et al., *Proc. Phys.-Math. Soc. Japan*, (*Nippon Sugaku-Butsuri Gakkaishi*) **22**, 940 (1940).

TABLE II

CORRECTION FOR THE INTENSITIES (METHOD I) ETHYL CAPRONATE IN CARBON TETRACHLORIDE CONCENTRATION 0.044 mol./l. PATH LENGTH 0.124 mm. BAND AT 1737 cm^{-1}

mechanical slit width mm.	0.13	0.17	0.23	0.29	0.225*
s_1 cm^{-1}	1.43	1.87	2.53	3.19	1.0 *
observed D_{max}	0.327	0.326	0.324	0.318	0.332*
$\Delta\nu^c_{1/2}$ cm^{-1}	15.6	15.7	16.0	16.2	15.5 *
for $y/2b_0=0.025$					
s_1+y cm^{-1}	1.82	2.26	2.92	3.58	
corrected D_{max}	0.330	0.330	0.331	0.328	
for $y/2b_0=0.05$					
s_1+y cm^{-1}	2.21	2.65	3.31	3.97	
corrected D_{max}	0.330	0.331	0.332	0.329	
for $y/2b_0=0.075$					
s_1+y cm^{-1}	2.58	3.02	3.68	4.34	
corrected D_{max}	0.332	0.332	0.333	0.331	
for $y/2b_0=0.10$					
s_1+y cm^{-1}	2.96	3.40	4.06	4.72	
corrected D_{max}	0.332	0.333	0.334	0.332	
for $y/2b_0=0.125$					
s_1+y cm^{-1}	3.33	3.77	4.43	5.09	
corrected D_{max}	0.334	0.335	0.336	0.335	
for $y/2b_0=0.0$					
$s_1+0.4$** cm^{-1}	1.83	2.27	2.93	3.59	
corrected D_{max}	0.331	0.331	0.332	0.329	

* These values are measured with a P-E. 112G grating spectrometer.

** These values are obtained using a triangular slit function, the term s_2 responsible for the finite resolving power of the prism is equal to 0.4 cm^{-1}.

TABLE III

CORRECTION FOR THE PEAK INTENSITIES (METHOD II) ETHYL CAPRONATE IN CARBON TETRACHLORIDE. CONCENTRATION 0.044 mol./l. PATH LENGTH 0.124 mm. BAND AT 1737 cm^{-1}

mechanical slit width mm.	0.13	0.17	0.23	0.29
s_1 cm^{-1}	1.43	1.87	2.53	3.19
observed D_{max}	0.327	0.326	0.324	0.318
observed D''_{max}	−0.009	−0.009	-0.008_5	-0.008_5
for $y=0.0$ cm^{-1}*				
coefficient a_2	0.279	0.428	0.715	1.074
corrected D_{max}	0.330	0.330	0.330	0.327
for $y=1.2$ cm^{-1}				
coefficient a_2	0.373	0.539	0.847	1.226
corrected D_{max}	0.330	0.331	0.331	0.328
for $y=1.6$ cm^{-1}				
coefficient a_2	0.468	0.648	0.978	1.380
corrected D_{max}	0.331	0.332	0.332	0.330
for $y=2.0$ cm^{-1}				
coefficient a_2	0.575	0.770	1.123	1.545
corrected D_{max}	0.332	0.333	0.334	0.331

* These values are obtained using a triangular slit function, the term s_2 responsible for the finite resolving power of the prism is equal to 0.4 cm^{-1}.

TABLE IV
ESTER C=O BANDS IN CARBON TETRACHLORIDE SOLUTION

Compounds	ν_{max} (cm^{-1})	E_{max} (1/mol. cm.)	$\Delta\nu^{1/2}$ (cm^{-1})	$A\times10^8$ (cm^2/molecule. sec.)
methyl formate	1735	730	10.5	142
methyl acetate	1748	715	12.6	143
ethyl acetate	1742	732	12.7	149
n-butyl acetate	1741	590	15.9	151
isoamyl acetate	1742	605	15.7	156
ethyl propionate	1739	560	15.6	137
ethyl capronate	1737	615	15.6	147
dimethyl oxalate	1752	1050	9.5	268
	1781	570	9.8	
diethyl oxalate	1747	1010	11.6	291
	1773	540	12.5	
diethyl malonate	1739	825	15.6	302
	1756	630	16.7	
diethyl succinate	1739	1180	15.7	285
di-2-ethylhexyl adipate	1737	1090	17.5	307
di-2-ethylhexyl azelate	1736	1130	17.2	325
di-2-ethylhexyl sebacate	1736	1130	17.0	297
diethyl maleate	1735	1000	20.0	302

observed absorbance and its second derivative, i. e.,

$$D^0_{max} = D_{max} - a_2(d^2D/d\nu^2)_{max} \qquad (8)$$

where a_2 is a coefficient determined by the slit function, and given by

$$a_2 = \frac{\int g(\nu,\nu')\nu^2 d\nu}{\int g(\nu,\nu')d\nu} \qquad (9)$$

The a_2 values* are represented for the cases of a triangular slit function whose base length is equal to twice the spectral slit width s as $s^2/12$, and for a trapezoidal slit function whose details are defined in the preceding section as $[(s_1+y/2)^4-(y/2)^4]/12s_1(s_1+y)$.

To obtain the true corrected intensity, the trial and error examination of the value of y should be made in a similar manner as described in the preceding section. An example of this process is carried out for the C=O stretching band of ethyl capronate, and shown in Table III, where the third and fourth rows show the observed peak intensities and their second derivatives, respectively. The good agreement among the corrected intensities is obtained when we assume the value of y to be ca. 1.6 cm^{-1}.

This method is attractive, because of the non-existence of the assumption on the band shape, but the process to obtain the second derivatives of absorbances is troublesome. Moreover, Eq. 8 is only a first approximation, and for the large values of absorbances, Eq. 8 should be extended to the fourth derivative. These two disadvantages are too serious, and in the last section of this paper this method is not adopted.

True Integrated Absorption Intensity.—As regards the integrated intensities, there are few to be discussed, and the extrapolation method proposed by Wilson and Wells[3] can be applied to the actual cases. Namely, true integrated intensity A is obtained as the limiting value of the intensity B, i. e.,

$$A = \lim_{ct\to0} B = \lim_{ct\to0} \frac{1}{ct}\int \log_e(T_0/T)d\nu \qquad (10)$$

where c is the concentration of the solute in molecules per $cm.^3$ of solution, t is the cell length in cm., and ν is the frequency in cycles per second. Integration of the band is carried out over the frequency interval of the four times the apparent band half width on either sides of the band center. Special correction for the residual area under the wings is ignored.

Results on the C=O Band of Esters.—Table IV gives the frequencies of the band maxima, the true molecular extinction coefficients at the peak, the true band half widths, and the true integrated absorption intensities of C=O stretching vibration bands of fifteen esters as measured in carbon tetrachloride solutions. These results show good agreement with the

* In the original paper[2], a_2 is determined experimentally. But this procedure is quite erroneous, and here a_2 is calculated from the assumed slit function.

values obtained by the other authors[8-10].

The mean values and their standard deviations of the peak and area intensities per one C=O group are computed for the seven monoesters as

$$(E_{group})_{max} = 647 \pm 73 \quad \text{l.mol.}^{-1}\text{cm.}^{-1},$$

$$A_{group} = 146.4 \pm 6.3 \times 10^{-8} \quad \text{cm}^2\,\text{molecule}^{-1}\,\text{sec.}^{-1},$$

and the mean value of area intensities per one C=O group for the fifteen mono- and di-esters is given by

$$A_{group} = 147.5 \pm 6.2 \times 10^{-8} \quad \text{cm}^2\,\text{molecule}^{-1}\,\text{sec.}^{-1}$$

The mean values of area intensities per one C=O group are similar for the mono- and di-esters, and in both cases, the standard deviations of area intensities are quite small. This fact is valuable for the group type analysis of esters.

8) R. R. Hampton and J. E. Newell, *Anal. Chem.*, **21**, 914 (1949).
9) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).
10) S. A. Francis, ibid. **19**, 942 (1951).

Experimental

A Perkin-Elmer Model 112 spectrometer with calcium fluoride prism and a cell of 0.124 mm. thickness, determined by the interference method, was employed. All of the esters were purified by the ordinary method and distilled. The boiling points of the purified materials were in good agreement with the literature values.

We wish to express our sincere thanks to Professor S. Mizushima and Assistant Professor T. Shimanouchi who permitted us to use the grating spectrometer.

The cost of this work has been partly defrayed by a grant from the Ministry of Education.

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Über die Einwirkung des Bromwasserstoffs und des Sauerstoffs auf α,β-ungesättigte Ketone. II. Bildung eines α-Diketons aus dem ungesättigten α-Bromketon durch Sauerstoffeffekt[1]

Von Hazime KASIWAGI

(Eingegangen am 3. März, 1958)

Die α,β-ungesättigten Arylketone sind allgemein sehr schwierig den Sauerstoffeffekt zu erleiden, während derselbe Effekt bei ihren α-bromsubstituierten deutlich bemerkt worden ist, was die Bildung der aromatischen Carbonsäure durch die Abspaltung an der Kohlenstoffkette dieser letzteren zur Folge hat. Einige Beispiele davon sind im vorigen Bericht[2] hingewiesen, bzw. bildet Benzoesäure sich durch diese Zersetzung des α-Bromchalkons und *p*-Toluylsäure aus 4'-Methyl-α-bromchalkon. Hier gehört es notwendig zur Frage, die Struktur der mit der aromatischen Carbonsäure paarweise gebildeten Verbindung oder ihrer Umwandlungsprodukte zu ermitteln, was aber unglücklicherweise dem Verfasser nicht gelungen ist. Da aber man ein α-Diketon als Reaktionsprodukt unter Versuchsbedingungen, worin der Sauerstoffeffekt sich beteiligt, erhalten konnte, hier sollen Betrachtungen über das Resultat der Versuche und den darauf begründeten Reaktionsmechanismus angestellt werden.

Man lässt den Bromwasserstoff auf die stark verdünnte Petroleumätherlösung des α-Bromchalkons (ω-Brom-ω-benzylidenazetophenons I) oder α-Brom-4'-methylchalkons (ω-Brom-4-methyl-ω-benzylidenazetophenons II) unter heftigem Sauerstoffstrom reagieren. Nach der Reaktion wäscht man die eine kleine Menge von Wasser abscheidende, gelbe Lösung mit Bicarbonatlösung, trocknet und dampft den Petroleumäther unter vermindertem Druck ab. Die gelbe Lösung scheidet den braungelben, öligen Rückstand ab, der beim Stehen allmählich schwarzgrün wird.

1) Eingebracht in der vierten Jahresversammlung der Japanischen Chemischen Gesellschaft, Tokyo, 1951.
2) Dieses Bulletin, **26**, 355 (1953).

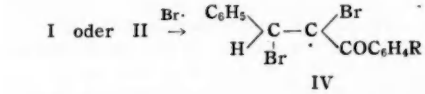
Beim Keton II, d. h. 4'-methylsubstituierten vom Keton I ist das Schwarzwerden durch Zersetzung nicht auffallender als beim ersteren und in den meisten Fällen kristallisiert die ölige Substanz sich zum Teil. Durch mehrmalige Umkristallisation mit wässrigem Alkohol wird diese Substanz gereinigt und kommt den bei 83.0~84.5°C schmelzenden, gelben Kristall zu geben. Der ermittelten Zahlen seines Molekulargewichts, Bromgehalts und seiner Reaktion nach, wodurch diese Verbindung unter Isolierung des Jods durch Einwirkung der Jodwasserstoffsäure reduziert wird, er zeigt sich als ein α-Diketon und zwar wird als *p*-Tolyl-ω-brombenzylglyoxal ($C_6H_5CHBrCOCOC_6H_4$-*p*-CH_3) (III) angesehen.

Um die Annahme zu versichern, dass die Struktur dieses gelben Kristalls wirklich der oben angedeuteten entspricht, hat man einen synthetischen Beweis ausführt, indem man den nach Beschreibung Jorländers[3] hergestellten *p*-Tolyl-benzylglyoxal mit Brom behandelt hat. Aus der Eisessiglösung der Reaktionsprodukte erhält man nach ihrer wiederholten Umkristallisation mittels wässriges Äthanols, einen gelben Kristall von Schmelzpunkt 84~85°C. Da jener gelbe Kristall mit dieser dargestellten Verbindung zusammengeschmolzen, keine Schmelzpunktserniederung zeigt, kann man annehmen, dass der erhaltene, gelbe Kristall mit dem bromsubstituierten vom *p*-Tolyl-benzylglyoxal übereinstimmt. Ungeachtet seiner Struktur als α-Diketon bildet der bromierte *p*-Tolyl-benzylglyoxal, mit *o*-Phenylendiamin behandelt, sich kein Chinoxalinderivat. Aber der nicht substituierte *p*-Tolyl-benzylglyoxal selbst gibt das Chinoxalin, das den von Jorländer angedeutete Schmelzpunkt und den der Theorie entsprechenden N-Gehalt hat. Angenommen, es bei der Frage nicht stehe, dass das Reaktionsprodukt mit der durch Einwirkung des Broms auf das oben erwähnte Glyoxal entstandenen Verbindung identisch sei, muss man aber darauf Aufmerksamkeit lenken, ob die Bromierung wirklich sich an α-Methylengruppe des Diketons vollzieht oder nicht. Jorländer nahm dem bromierten α-Diketon die Struktur von der oben genannten Formel III[4] an. Dieses Umstands und der Reduzierbarkeit des Reaktionsprodukts durch Jodwasserstoffsäure nach kann man mit Bestimmtheit annehmen, dass es zwar die Struktur III hätte. Das entsprechende α-Diketon konnte man aus den Reaktionsprodukten des nicht 4-methylierten, ungesättigten Bromketons I nicht erhalten, da der aus der Reaktionsflüssigkeit durch Abdampfen des Lösungsmittels unter vermindertem Druck hintergebliebene Rückstand durch Zersetzung merkwürdigerweise schwarz wird und die unverkennbare Substanz nicht gibt. Aber die von den sauren Stoffen durch Ausschütteln mit Bicarbonat befreite Lösung nimmt eine dem α-Diketon eigentümliche gelbe Farbe an.

Unter Umständen erhielt man einen anderen Kristall aus den Umwandlungsprodukten des nicht 4-methylierten Ketons I. Mit wiederholter Umkristallisation mittels wässriges Äthanols wird der Kristall weiss und allmählich schwerer löslich in Äthanol, und erweist sich als das Dibromid des Phenylstyrylketons, und zwar als das von tieferem Schmelzpunkt. In manchen Fällen wurde das entsprechende Dibromid auch bei der Reaktion betreffs des ungesättigten Bromketons II durch das ähnliche Verfahren erhalten. Bei dem Falle aber, worunter man das Dibromid empfangte, wurde es nicht gelungen, α-Diketon zu isolieren.

Diese Tatsache zusammengenommen, kann man schliessen, dass das ungesättigte Bromketon I oder II unter den Bedingungen, die für den Sauerstoffeffekt seinen Auftritt verantwortlich sind, die saure Substanz und den augenreizenden Stoff von unbekannter Struktur, wie gesagt im vorigen Bericht, gleichzeitig mit dem α-Diketon oder andernfalls dem Ketondibromid gäbe. Solche Ketondibromide jedoch auch für die normalen Additionsprodukte des Bromwasserstoffs zum Keton I und II gelten, weist die Beweisführung ihrer Bildung allein die Mitwirkung eines Mechanismus von der anomalen Addition nicht auf.

Aber wenn eine von dem Sauerstoffeffekt herrührende Reaktion wirklich stattfinden könnte, würde das Keton als sich mit dem Bromatom zuerst ein organische, freie Radikal zu bilden, vermutet, folgendermassen;

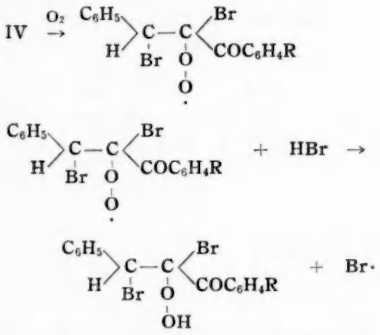


IV

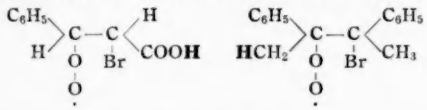
Als die alternierende Form des freien Radikals kommt es zwar in Betracht eine von der Struktur, worin das Bromatom

3) *Ber.*, **50**, 418 (1917).
4) Jorländer, loc. cit..

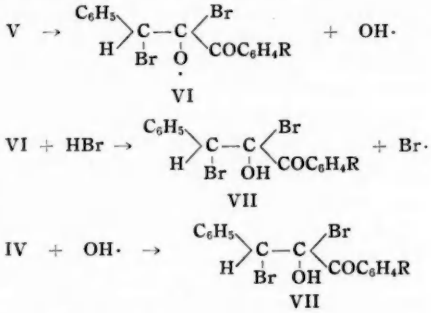
sich an das α-ständigen, ungesättigten Kohlenstoffatom addieren könne, aber darf solche Struktur im Vergleich mit den oben angestellten von ihrer minderen Beständigkeit aus wohl als die geeignetere Form nicht angesehen werden[5]. Das einmal gebildete Radikal IV, der Einwirkung des Sauerstoffs und des Bromwasserstoffs ausgesetzt, geht in ein Hydroperoxyd V über.



Obwohl man hier bezüglich der Bildungsweise des Hydroperoxyds vermutete, dass das Wasserstoffatom, das von Peroxydradikal empfangt wird und in die Zusammensetzung eingeht, seinen Ursprung ausschliesslich im reagierenden Bromwasserstoff hätte, wenn die freien Radikale das aktive Wasserstoffatom enthalten, auch dieses letzteren könnte an die Bildung des Hydroperoxyds teilnehmen. So kann man als das dafür geltende Beispiel betrachten, dass das bei der genannten Reaktion der Zimtsäure gebildete Peroxydradikal einen aktiven Carboxylwasserstoff enthält und die intramolekulare Umlagerung ihm als möglich angesehen wird[6]. Das Wasserstoffatom der verzweigten Methylgruppe von Dimethylstilben bediene sich auch als solches. In diesem Falle kann wahrscheinlich seine intermolekulare Austausch stattfinden[7].

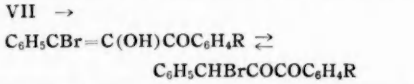


Das unbeständige Hydroperoxyd gibt durch Zersetzung das freie Hydroxylradikal und ein anderes sauerstoffhaltige Radikal VI. Dieses Radikal, die Einwirkung des Bromwasserstoffs erleidet, gibt das Hydroxyd VII unter Wiederherstellung des Bromatoms. Daher bietet auch diese Stufe von Reaktion die der Fortpflanzung der Reaktionskette dar. Das Hydroxyd mag auch durch unmittelbare Vereinigung des eigentlichen, freien Radikals IV mit dem Hydroxyl gebildet werden.



Im Radikal VI übrigens befindet seine Bindung zwischen den Atomen des Carbonylkohlenstoffs und seines α-ständigen wegen der grossen Elektronenaffinität des Sauerstoffs, sich in einem schwächerem Zustand, was ihr Auflösen zur Bildung der aromatischen Säure und nicht identifizierter Stoffe von augenreizender Eigenschaft zur Folge haben kann.

Die Bildung α-Diketons beruht auf der Abspaltung des Bromwasserstoffs aus dem Hydroxyd VII, da hier dieses als recht unbeständig angesehen wird, um es in einem selbständigen Zustand zu erkennen.



Die der Form VII entsprechende Hydroxylverbindung sei nicht immer unbeständig, so ist es in gewissen Fällen gelungen worden, die zuständige Hydroxylverbindung als solche wirklich zu identifizieren. Dafür gilt die Isolierung der α-Hydroxy-β-brombuttersäure aus den Reaktionsprodukten der Krotonsäure mit dem Bromwasserstoff und dem Sauerstoff[8].

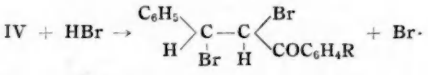
Die andere Möglichkeit von der Formation α-Diketons, die hier in Betracht kommen müsste, wäre die Anhäufung des Broms an die Doppelbindung des eigentlichen, ungesättigten Ketons und die nachherige Verseifung des so entstandenen Tribromids.

Zur Prüfung dieser Bildungsweise α-Diketons stellt man das Tribromid durch

5) F. R. Mayo und C. Walling, *Chem. Revs.*, **27**, 373 (1940).
6) O. Simamura und M. Takahashi, Dieses Bulletin, **22**, 60 (1949).
7) H. Suzuki, O. Simamura und T. Ichihashi, ebenda, **27**, 234 (1954).
8) O. Simamura, ebenda, **17**, 327 (1942).

Addition des Broms zum Keton II. Das so erhaltene Tribromketon bietet einen bei 104.5～106°C schmelzende, weissen Kristall dar und ist zwar genügend beständig, mit Wasser oder Alkali behandelt, keine Veränderung zu erleiden. Freilich kann man eine Schmelzpunktserniederung beobachten. Bezüglich des Ketons I wird das entsprechende Tribromketon als der bei 202～4°C schmelzende, ebenfalls weisse Kristall erhalten. Daraus kann man ersehen, dass α-Diketon die Ursache seiner Bildung über das Tribromketon der Verseifung dieses letzteren nicht zugeschrieben wird.

Die Gelegenheit für das erste Radikal IV, mit dem Bromwasserstoff zu begegnen, bildet eine andere Fortpflanzungsstufe der Reaktionskette, die Formation des Dibromketons vom tieferen Schmelzpunkt verursacht, das übrigens auch als gebildet durch elektrophile Addition des Bromwasserstoffs auf das ungesättigte Bromketon betrachten werden könne.



Wie erwähnt im vorigen Bericht, bei der Reaktion α-Bromchalkons ist der Ertrag der aromatischen Säure ungefähr dreimal soviel als bei seinem 4′-Methylderivat. Die Ursache davon sei vielleicht dem Umstand zuzuschreiben, dass bei dem 4′-Methylderivat das sauerstoffhaltige Radikal VI infolge seiner Stabilisierung durch die Vergrösserung seiner Delokalisierungsenergie, damit die Gegenwart der 4′-Methylgruppe wegen ihrer Hyperkonjugierung mit dem Benzolkern zustandekommt, sich im beständigeren Zustand im Vergleich mit dem aus nicht substituierten Bromketon entstandenen Radikal befindet, was dem Radikal VI das Hydroxyd, die Muttersubstanz α-Diketons zu bilden hilft. Daraus kann man ersehen, dass der verminderte Ertrag der aromatischen Säure durch Zersetzung des Radikals VI im Falle von der Reaktion des 4′-Methylderivats der leichten Isolierbarkeit α-Diketons entspreche.

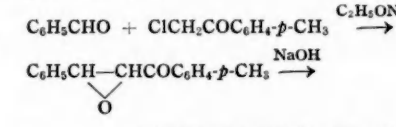
Beschreibung der Versuche

Ungesättigte Bromketone I und II. — Ihre Darstellung; schon erwähnt im vorigen Bericht[2].

Isolierung des gelben Kristalls.—Löst man 2.00 g ω-Brom-4′-methyl-ω-benzylidenazetophenon in bei 75～90°C siedendem Petroleumäther auf und leitet den Bromwasserstoff und den Sauerstoff ein. Die Lösung wird nach der Reaktion zur Beseitigung der sauren Stoffe mit Carbonatlösung ausgeschüttelt, mit wasserfreiem Natronsulfat getrocknet und dann das Lösungsmittel unter vermindertem Druck abdampfen lassen. Der Rückstand beträgt 2.5 g und ist ein gelbe, ölige Stoff von stürmisch augenreizendem Geruch, der durch Abspaltung von Bromwasserstoff allmählich schwarzgrün wird. Dieser ölige Körper ist in Petroleumäther leichter löslich. Wenn man diesem öligen Stoff mit wenig Äthanol versetzt und ihn unter Kühlung mittels Eiswassers stehen lässt, so kristallisiert es sich allmählich aus. Das erhaltene Produkt ist der bei 78～81°C schmelzende, weisse Kristall, der 1.10 g beträgt. Der Schmelzpunkt desselben steigt auf nach dreimaliger Umkristallisation mittels Äthanols bis auf 83.0～84.5°C. Es riecht augenreizend keineswegs mehr. Die Anwesenheit des Halogens lässt durch Beilsteinsche Prüfung erkennen. Mol. Gew. nach Rast und Br%: 315, 25.05; ber. für $C_{16}H_{13}O_2Br$ 317, 25.23.

Reaktion mit o-Phenylendiamin. Wenn man zur 3 ccm Äthanollösung von 0.1 g des Kristalls mit 0.3 g *o*-Phenylendiamin versetzt, so färbt sich die Lösung sofort rot und, gibt, mit Wasser verdünnt, ein rote Öl, das, mit Äthanol oder Benzol-Ligroin behandelt, sich nicht kristallisieren kann.

Darstellung des p-Tolyl-ω-brombenzylglyoxals. Um die Übereinstimmung des aus der Reaktionsflüssigkeit erhaltenen mit dem *p*-Tolyl-ω-brombenzylglyoxal zu versichern, stellt man zuerst den nicht bromierten Glyoxal dar, indem man den Benzaldehyd mit dem Methylphenazylchlorid durch Natriumäthylat kondensieren lässt, dann das so erhaltene Oxydäthan mit Natronlauge in Äthanol und nachher mit Salzsäure behandelt, lautet es wie folgt:



Das rohe Glyoxal, aus wässrigem Methanol auskristallisiert, bietet einen bei 89°C schmelzenden, schwachgelb gefärbten Kristall dar. Löst man sodann 0.71g dieses Kristalls in 4ccm Methanol auf und versetzt mit 0.32 g *o*-Phenylendiamin, so färbt die Lösung rot. Wird die durch Hinzufügen mit wenig Wasser weiss getrübte Reaktionsflüssigkeit solange auf dem Wasserbad erhitzt, bis sie klar gemacht wird, und stehen zum Abkühlen lassen, so scheidet das Chinoxalin als weisser Kristall sich von der Lösung ab. Der Kristall, dreimal mit wässrigem Äthanol umkristallisiert, schmilzt bei 112.0～112.5°C. N%: Beob. 9.08; ber, für $C_{22}H_{18}N_2$ 8.92. Man lässt 1 Mol. Äquiv. Broms (1.2 g) unter Kühlung mit Eis in die Lösung allmählich eintropfen. Wird das Ganze ins Wasser eingegossen, so sinkt das Reaktionsprodukt als rote, ölige Tropfen auf den Boden. Wenn man es mit Äther aufnimmt,

zuerst mit Bicarbonatlösung, dann mit Wasser auswäscht, trocknet und das nach dem Wegdampfen des Lösungsmittels nachgebliebene Öl mit Kältemischung stark abkühlt, so kristallisiert es sich langsam. Das so erhaltene Reaktionsprodukt ist ein gelbe, bei 82.5～84.0°C schmelzende Kristall, der 1.7 g beträgt. Dieser Kristall, mit wässrigem Methanol umkristallisiert, kommt bei 84～5°C zu schmelzen, und mit dem oben erwähnten aus der Reaktionspetroleumätherlösung erhaltenen, ebenfalls gelben Kristall zusammengeschmolzen, zeigt keine Schmelzpunktserniederung, d. h. schmilzt bei 84～5°C. Wenn man ferner einen Teil desselben nimmt und zu seiner Äthanollösung mit der kleinen Menge von Kaliumjodidlösung versetzt, so scheidet das Jod nach Ansäuerung der Lösung sich von derselben ab, was man aus der Entfärbung durch Einwirkung des Natriumthiosulfatlösung erkennt. Daraus kann man schliessen, dass sowohl die Bromierung am α-Kohlenstoffatom des p-Tolyl-ω-benzylglyoxals stattfindet wie das eine von der unter den Bedingungen, die für den Auftritt des Sauerstoffeffekts verantwortlich sind, aus dem ungesättigten Bromketon II entstandenen Produkten mit dem p-Tolyl-ω-brombenzylglyoxal übereinstimmt.

Die Einwirkung des Broms auf die α-Bromketon I und II. — Man löst 1.10 g Bromketon II in 5 ccm Chloroform auf und lässt 0.59 g Brom in die Lösung hinzufügen. Während des Eintropfens verschwindet die Farbe des Broms nicht, wird aber die Reaktion unter Entfärbung der Lösung hervorgerufen, wenn man die Lösung auf dem Wasserbad erwärmt. Nach dem Abdampfen des Lösungsmittels löst man das Produkt im ein wenig Chloroform hinzugefügten Äthanol auf und lässt die Lösung eiskalt stehen. Auf solche Weise gewinnt man 1.0 g einen farblosen Kristall. Der Schmelzpunkt desselben, wenn es mit dem genannten Lösungsmittel wieder umkristallisiert, wird zu 104.5～106°C. Obwohl man zu diesem Produkt aus den ermittelten Zahlen durch Elementaranalyse (beob.: C, 41.15; H, 2.53; Br, 51.87. ber. für $C_{16}H_{13}OBr_3$: C, 41.65; H, 2.82; Br, 52.03%) die dem Dibromid vom ungesättigten α-Bromketon entsprechenden Zusammensetzung zuschreiben mag, sollte man das von diesem Tribromketon sekundär durch Alkali verwandelte Produkt nicht ansehen, weil dieser Kristall, mit Sodalösung geschüttelt, keine Veränderung erleidet. Die gleiche Additionsreaktion ist auch bei dem ungesättigten Bromketon I durchzuführen. D. h. wenn man dieselbe Reaktion des 0.77 g Ketons mit 0.45 g Brom in Chloroformlösung vollzieht, so erhält man den 0.72 g bei 102～4°C schmelzenden, farblosen Kristall (Br: Beob. 53.94; ber. für $C_{15}H_{11}OBr_3$, 53.66%). Auch wird dieser Stoff durch schwachem Alkali nicht angegriffen.

Hydrobromide der Ausgangsketone. — Unter den gleichen Bedingungen, als man betreffs der Isolierung des gelben Kristalls von α-Diketon am Anfang dieser Beschreibung angestellt hat, andernfalls wird aber das Hydrobromid des eigentlichen, ungesättigten Bromketons als ein Reaktionsprodukt aus der Reaktionsflüssigkeit isoliert. Hierbei ist die Ursache nicht klar, was für ein Zustand die Unbestimmtheit des isolierten Produkts veranlassen soll. Ein Beispiel wie folgt: Löst man 3.68 g Keton I in 145 ccm bei 62～75°C siedendem Petroleumäther auf und lässt darauf den Bromwasserstoff unter Durchleitung des heftigen Sauerstoffstroms eiskalt für 3.5 Std reagieren. Nach der Reaktion die Lösung, durch Bicarbonatlösung von den sauren Stoffen befreit, nimmt eine auffallende, gelbe Farbe an. Man nimmt einen kleineren Teil davon, lässt das Lösungsmittel unter vermindertem Druck abdestillieren und den nachgebliebenen Rückstand in Eiskasten stehen. Der Kristall ist in Äthanol recht schwer löslich, wird durch Umkristallisation aus demselben Lösungsmittel gereinigt und kommt bei 116～120°C zu schmelzen. Dieser Stoff ergibt aus der Mischprobe sich als das Dibromid des ω-Benzylidenazetophenons von tieferem Schmelzpunkt, d. h. das bei 120～1°C schmelzenden. In ähnlicher Weise kann man aus 2.0 g Bromketon II 1.2 g des weissen Kristalls erhalten, der, mit dem bei 156.5～157.5°C schmelzenden Dibromid des 4-Methyl-ω-benzylidenazetophenons[9] zusammengeschmolzen, keine Schmelzpunktserniederung zeigt. Bei diesem Falle aber, abweichend von dem Falle, worin das α-Diketon isoliertworden ist, tritt ein merkwürdigeres Schwarzwerden der Reaktionsflüssigkeit während ihrer Behandlung auf.

Zusammenfassung

Aus der Untersuchung über die Einwirkung des Bromwasserstoffs und des Sauerstoffs auf α-Brom-α, β-ungesättigten Arylketone ergeben sich auch das α-Diketon und die Hydrobromide der Ausgangsketone neben den im vorigen Bericht mitgeteilten, aromatischen Säuren als die Reaktionsprodukte. So erhält man aus ω-Brom-ω-benzylidenazetophenon und ω-Brom-4-methyl-ω-benzylidenazetophenon ihr Hydrobromid und aus dem letzteren auch ein α-Diketon, bzw. p-Tolyl-ω-brombenzylglyoxal. Darauf hin kann man annehmen, dass die Reaktion einem durch die freien Radikale hervorgebrachten Kettenmechanismus gemäss läuft. Von solchen freien Radikalen werden sowohl das aus dem Ausgangsstoff unter Vereinigung desselben mit Bromatom gebildeten Radikal $C_6H_5CHBr\dot{C}BrCOC_6H_4R$ als das aus ihm über das Hydroperoxyd durch die Abspaltung des freien OH· verwandelten, sauerstoffhaltigen Radikal $C_6H_5CHBrCBr(O\cdot)COC_6H_4R$ für besonders wichtig angesehen, weil sie als die Zwischenstoffe der Reaktion die Natur der Produkte bestimmen.

9) C. Weygaand und A. Matthes, *Ber.*, **59**, 2247 (1926); siehe auch die Mitteil. I, S. 356, Anm. 7.

Hinzufügen ist dazu, dass die Ertragsverminderung der durch die dem Sauerstoffeffekt zugeschriebene Zersetzung der Kohlenstoffkette der Ketone abgespaltenen, aromatischen Säuren bei der Strukturabänderung des Substrats von α-Bromketon I zu seinem 4'-methylierten(II) wahrscheinlich in Folge der Stabilisierung des oben angestellten, sauerstoffhaltigen Radikal durch die Gegenwart des letztgenannten Substituenten mit seinem Hyperkonjugierungseffekt hervorgerufen werde.

Zum Schluss muss der Verfasser den Herren Professor Y. Urushibara und Professor O. Simamura an der Universität zu Tokyo für ihre freundlichen Leitungen den herzlichen Dank aussprechen.

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*The Separation of Polythionates with Anion-Exchange Resins**

By Akira IGUCHI

(Received March 14, 1958)

The separation of di-, tri-, tetra- and penta-thionates is very difficult by an ordinary analytical method. In the present study, the author applied the anion-exchange chromatography to this separation. First, the distribution coefficients, K_d, of polythionates to the anion-exchange resin were measured and, by the use of these results, polythionates were separated with satisfactory results.

Experimental

Materials. — Anion-exchange resin, Dowex 1-X2, X4 and X8 of mesh size 50~100 were used in air dried state and in chloride form.

The following polythionates were synthesized by the usual methods described in text books[1,2].

Sodium dithionate was prepared by the reaction of sodium sulfite with silver nitrate[3].

Sodium trithionate was obtained by passing sulfur dioxide into a solution containing both sodium thiosulfate and bisulfite with a small amount of sodium arsenite. Potassium salt was obtained by the double decomposition of sodium salt with potassium acetate[4].

Sodium tetrathionate was prepared by mixing sodium thiosulfate with iodine in the granular state[5].

Potassium pentathionate was prepared by the reaction of concentrated hydrochloric acid with a solution containing sodium thiosulfate and a small amount of sodium arsenite at −10°C[6].

Procedure. *Analysis of polythionates.*—Sodium dithionate was oxidized by potassium bromate in acidic solution and the formed sulfate ion was determined by the usual gravimetric method. The purity of this salt was also determined by heating and decomposing it into sodium sulfate. The sodium sulfate was determined gravimetrically[7,8].

Potassium trithionate was titrated with potassium iodate[9]. Its purity was also determined from the decrease of weight on conversion into potassium sulfate by heating[10].

Sodium tetrathionate and potassium pentathionate were titrated with potassium iodate as in the case of trithionate[9]. The purity of these salts was also determined through the reaction with sodium sulfite. The thiosulfate ion thus formed was determined by iodimetric titration after masking the residual sulfite ion with formalin[11].

The results of these analyses showed that these salts were pure enough for the purpose of this study.

Measurement of Distribution Coefficients in Various Concentrations of Hydrochloric

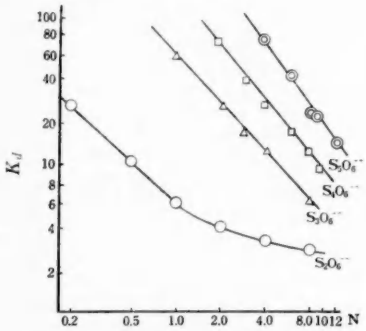
* This paper was presented before the Autumn Meeting of the Chemical Society of Japan held on Nov. 23, 1957 in Tokyo.

1) W. G. Palmer, "Experimental Inorganic Chemistry", Cambridge Univ. Press, England (1954), p. 365.
2) T. Inouye, "Inorganic Preparative Experiments" (Mukikagaku Seizojikken), Shokabo, Tokyo (1956), p. 96.
3) H. Baubigny, *Ann. chim. phys.*, (VIII), **20**, 5 (1910).
4) A. Kurtenäcker and K. Matejka, *Z. anorg. allgem. Chem.*, **193**, 367 (1930).
5) N. v. Klobukow, *Ber.*, **8**, 1871 (1885).
6) A. Kurtenäcker and W. Fluss, *Z. anorg. allgem. Chem.*, **210**, 125 (1933).
7) C. Mayr and I. Szentpaly-Peyfuss, ibid., **131**, 203 (1924).
8) W. C. de Baat, *Rec. trav. chim., Pays-Bas*, **45**, 237 (1926); *Chem. Zentr.*, **97**, (I) 3133 (1926).
9) A. Kurtenäcker et al., *Z. anorg. allgem. Chem.*, **224**, 399 (1935).
10) H. Stamm, K. Goejring and U. Feldmann, ibid., **250**, 226 (1942).
11) F. Forster and K. Centner, ibid., **157**, 45 (1926).

Acid.—The measurement of distribution coefficients K_d was carried out by the column method. The K_d values of the ions were calculated from the volume of the eluant, using the following equation:

$$K_d = (V-i)/M$$ [12]

where K_d (cc./g.) is the distribution coefficient, V (cc.) the volume of eluant passed through the column until the concentration of solute in the effluent becomes maximum, i (cc.) the interstitial volume of the column and M (g.) the weight of the resin.



Concentration of hydrochloric acid

Fig. 1. Relationship between K_d and the concentration of hydrochloric acid in the eluant.

Each column contains 0.5~2.0 g. of the resin, Dowex 1-X2 in chloride form. The flow rate is adjusted to less than 0.1 cc./min. The relation between K_d and the concentration of hydrochloric acid (C) in the eluant is shown in Fig. 1. A nearly linear relationship between $\log K_d$ and $\log C$ is recognized. The values of K_d of polythionate ions for the same concentration of hydrochloric acid increase with the increase of the numbers of sulfur atom in the ion. The curves for these polythionates were almost parallel to one another. The gradient of these curves was not so great as two, but almost unity; hence as was studied by M. Honda[13], these polythionate ions may exist in these acidic solutions as $HS_nO_6^-$, n being 2~5.

Results and Discussion

The Effect of pH and the Pore-size of Ion-Exchange Resins on the Distribution Coefficient. — i) *pH.* — By using sodium chloride solution, or sodium chloride solution containing ammonia as an eluant in place of hydrochloric acid, the values of K_d in different pH** were measured. The concentrations of sodium chloride used were 0.5 mol./l. for dithionate and 4.0 mol./l. for other polythionates. The results are shown in Fig. 2. The K_d was almost independent of pH.

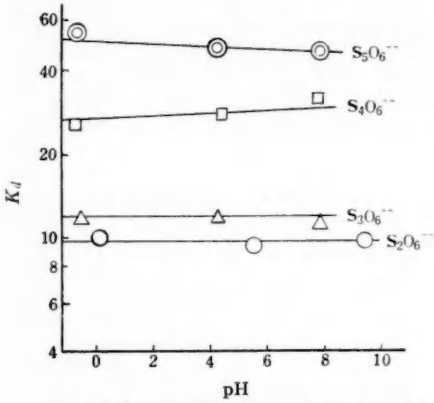


Fig. 2. Relationship between K_d and the pH of eluant. The concentration of hydrochloric acid used as the eluant was 0.5 N for dithionate and 4 N for tri-, tetra- and penta-thionates.

ii) *Pore-size.*—The resins of different X numbers were employed in place of X2 resin to observe the effect of pore-size. The K_d values for dithionate in 1.0 N hydrochloric acid, trithionate in 3.0 N hydrochloric acid, tetrathionate in 6.0 N hydrochloric acid and pentathionate in 9.0 N hydrochloric acid were measured by the elution method using Dowex 1-X2, -X4 and -X8 resins. The results are shown in

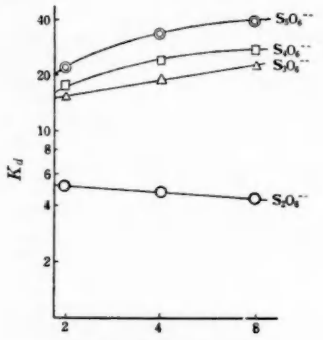


Fig. 3. Relationship between K_d and the X numbers of resins. The concentration of hydrochloric acid used as the eluant was 1 N for dithionate, 3 N for trithionate, 6 N for tetrathionate and 9 N for pentathionate.

12) M. Honda, *Japan Analyst* (*Bunseki Kagaku*), **2**, 155 (1953).
13) M. Honda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 361 (1951).
** pH of the solution was measured with a glass electrode pH-meter, Type 43, made by Iio Denki Co..

TABLE I
THE ANALYSIS OF MIXED SAMPLES

Thionates	Sample 1 Added	Sample 1 Observed		Sample 2 Added	Sample 2 Observed	
	millimole	millimole	%	millimole	millimole	%
Dithionate	0.124	0.122	98.6±2.0	0.100	0.0987	98.7±2.0
Trithionate	0.0584	0.0560	96.0±5.0	0.0707	0.0690	97.4±4.0
Tetrathionate	0.0650	0.0650	100 ± 2.6	0.0336	0.0328	97.7±2.3
Pentathionate	0.0339	0.0343	101 ± 2.8	0.0338	0.0333	98.6±2.3

TABLE II
THE ANALYSIS OF WACKENRODER'S LIQUID

	Sample A Observed value millimole	Sample A Mol. %	Sample B Observed value millimole	Sample B Mol. %
Sulfide, Sulfite, Thiosulfate	0.00	0.00	0.00	0.00
Sulfate	6.77×10^{-2}	23.2	4.90×10^{-2}	20.5
Dithionate	2.58×10^{-3}	0.89	3.75×10^{-3}	1.57
Trithionate	5.82×10^{-2}	19.9	5.63×10^{-2}	23.7
Tetrathionate	9.12×10^{-2}	31.2	4.83×10^{-2}	32.9
Pentathionate	5.40×10^{-2}	18.5	4.59×10^{-2}	19.2
Higher thionates	7.70×10^{-3}	2.63	4.87×10^{-3}	2.04

Fig. 3. Slight increase of K_d with the increase of X number was recognized in cases of tri-, tetra-, and penta-thionates, though the difference is not so great. In the case of higher polythionates, elongation of the tail part was observed in the elution process.

Separation of Polythinonates by the Column Method.—The polythionates may be separable because they show different K_d values as shown in Fig. 1. The used column contains 2.16 g. of Dowex 1-X2 and the size of the column is about 0.90 cm. in diameter and about 11 cm. in length. First the dithionate is eluted with 1 N hydrochloric acid. When any other oxy-acids of sulfur than polythionates are contaminated in the sampe to be analyzed, they are eluted out at this stage before the dithionate appears in the eluant. Then trithionate was eluted with 3 N hydrochloric acid, tetrathionate with 6 N and pentathionate with 9 N hydrochloric acid successively.

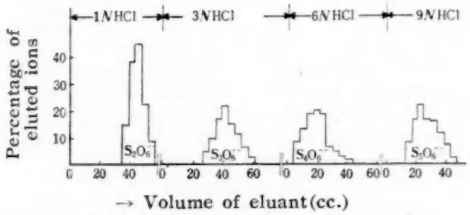


Fig. 4. Elution curve of a mixed sample. The flow rate was 0.5 cc./sec.

The amount of eluted dithionate is determined by gravimetric method and tri-, tetra- and penta-thionates are by the titration with standard potassium iodate solution as described in the experimental part.

One of the typical clean-cut separation of mixed sample is shown in Fig. 4.

Analysis of Mixed Samples. — The method of separation, described above, was applied to the mixture of the known amounts of polythionates and the results are shown in Table I, the mean values of the triplicate experiments being given.

When the sample contains other oxy-acids of sulfur, (e.g., sulfate, sulfite, etc.), they are eluted prior to the elution of dithionate, and are determined separately.

Analysis of Wackenroder's Liquid[14,15]**.** —This method of separation was applied to the determination of the composition of Wackenroder's liquid. The composition of the liquid, however, may change owing to the preparation method, and further, it contains a large amount of suspended sulfur which interferes with the analytical process. Two samples made by the following methods were analyzed.

i) *Sample A.* — This sample was prepared by dissolving hydrogen sulfide into

14) H. W. F. Wackenroder, *Ann. chim. phys.*, (III), **20**, 144. (1847).
15) H. Debus, *Ann.*, **244**, 76, (1888).

saturated aqueous solution of sulfur dioxide at 0°C. Hydrogen sulfide was passed twice after an interval of 48 hours, and the solution was left standing 38 days at room temperature (20~15°C). Then the suspended sulfur in the liquid was caused to coagulate by the addition of an equal volume of 1.00 M ammonium chloride solution and filtered off. A portion of the filtrate was titrated with standard iodine solution after being acidified with acetic acid, but the presence of sulfide, sulfite or thiosulfate was not recognized. With another portion of the filtrate, the content of sulfate was determined by the gravimetric method in the form of barium sulfate.

The ion-exchange chromatographic method used for the analysis of Wackenroder's liquid is the same as that used for the known mixed sample, but after the elution of pentathionate with 9 N hydrochloric acid, there remained only a small amount of polythionate which could be eluted only by 12 N hydrochloric acid. Although it was difficult to determine this species, the values in Table II were calculated on the assumption that this species would be hexathionate.

The quantity of dithionate was calculated from the difference between the amount of barium sulfate obtained from the first effluent after oxidation and the amount of the barium sulfate directly from the original sample solution.

ii) *Sample B.*—Sample B was prepared by the same method as that for Sample A, but the solution was left standing only 11 days after passage of hydrogen sulfide. As the suspended sulfur coagulates with difficulty, 1.5 times (by volume) of 1.00 M ammonium chloride solution was mixed before filtration of the sulfur.

The results of the analysis of 1 cc. of the original Wackenroder's liquid are given in Table II.

Summary

1) The distribution coefficient of di-, tri-, tetra-, and penta-thionates between anion-exchange resins and hydrochloric acid solution was measured. The adsorbability of the polythionates increases with the number of sulfur atoms in the ion, i. e. pentathionate>tetrathionate>trithionate>dithionate.

2) The separation of polythionates was accomplished by the anion-exchange chromatography by the use of hydrochloric acid in various concentrations as the eluant.

3) The application of anion-exchange chromatography to the analysis of Wackenroder's liquid was studied.

The author expresses his gratitude to Professor T. Shirai, Dr. Y. Yoshino and to his colleagues in the laboratory for their suggestions throughout the work.

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*The Separation of Sulfate, Sulfite, Thiosulfate and Sulfide Ions with Anion-Exchange Resins**

By Akira IGUCHI

(Received March 14, 1958)

Several methods of analysis of the mixture of sulfite, thiosulfate and sulfide ions have been reported by some researchers[1], most of which are based on the method of titration without separation of these components. In this study the author has applied the anion-exchange chromatography to the mutual separation of the above-mentioned oxy-acids of sulfur and sulfide, obtaining satisfactory results.

* This paper was presented before the 6th Annual Meeting of Japan Society for Analytical Chemistry held on Oct. 19, 1957 in Kyoto.

1) For example, A. Kurtenäcker et al., *Z. anorg. allgem. Chem.*, **161**, 201 (1927).

Experimental

Materials. — *Anion-exchange resins.* — Diaion SA # 100, a strongly basic type resin (polystyrene-

divinyl benzene quaternary amine) prepared by Mitsubishi Kasei Co. was used. It is of mesh size 100~200 in beads (nitrate form).

Sodium thiosulfate.—The guaranteed reagent of Junsei Chemicals Co. was used. The iodometric titration showed that this sample did not contain impurities which would interfere with the experiment.

Sodium sulfate.— The guaranteed reagent of Junsei Chemicals Co. was used. The result of gravimetric analysis showed that this sample was sufficiently pure for the purpose of this study.

Sodium sulfite and sodium sulfide.—Aqueous solutions of both salts are oxidized easily, but the decrease of the concentration was found to be less than about 1% for sulfite, and less than 2% for sulfide during the process of separation (about 6~10 hours). The quantity of sulfate in the original sulfite solution was determined from the difference between the quantity of sulfite titrated iodometrically and that of sulfate plus sulfite which was weighed gravimetrically in the form of barium sulfate after oxidizing the sulfite into sulfate. The amount of impurity contained in the sulfide solution newly prepared was found to be negligible.

Procedure.—*Measurement of distribution coefficient.*—For the separation of these readily oxidizable anions, it is not desirable to use resins in the nitrate form, as the nitrate acts as an oxidant. On the other hand, the chloride solution is not suitable for the elution of these anions, as the tail part of the elution curve becomes long. Solution of sodium or ammonium nitrate plus ammonia was found to be an excellent eluant, the oxidizing effect not appearing in these conditions. In a neutral solution, a slight decomposition of sulfite and sulfide was recognized, especially in contact with resins in nitrate form. This decomposition may be due to the catalytic action of resins.

The measurement of distribution coefficient, K_d, was made by the column method. The K_d values of the ion were calculated from the volume of eluant by using the following equation:

$$K_d = (V - i)/M$$ [2]

where K_d(cc./g.) is the distribution coefficient, V (cc.) the volume of eluant passed through the column until the concentration of solution in the effluent becomes maximum, i(cc.) the interstitial volume of the column and M(g.) the weight of the resin.

Each resin column contains 1 to 3 g. of Diaion SA ♯100. The size of the column is 7.0 mm. in diameter. The flow rate is less than 0.1 cc./min.. The eluant was aqueous solution of sodium nitrate, but the solution of ammonium nitrate containing ammonia was also used for sulfite ion.

2) M. Honda, *Japan Analyst (Bunseki Kagaku)*, **2**, 155 (1953).
3) M. Honda, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **72**. 361 (1951).

Results and Discussion

Relations Between the Distribution Coefficient and the Concentration of Nitrate Ion in the Eluant.—The mean values of the distribution coefficient of triplicate experiments are shown in Fig. 1. From these data a linear relationship between $\log K_d$ and the concentration of nitrate ($\log C$) is recognized, especially in the region of low concentration. The curves for sulfite, thiosulfate and sulfate ions are nearly parallel, and the slope is about 2 at 0.1~0.2 mol./l., hence, as Honda discovered and reported[3], they must be doubly charged ions. In the case of sulfide, the slope of the line is nearly unity, suggesting the probable presence of HS^- ion even in a neutral solution. From the data in Fig. 1, thiosulfate, sulfate and sulfite may be separable using 0.1 mol./l. nitrate solution as an eluant.

The Relation between pH and Distribution Coefficients. — The distribution coefficient K_d of ions of polybasic acids may change with the variation of pH. Accordingly the relationship between pH and K_d was checked in the range of pH 7~11. The buffer solution, prepared by

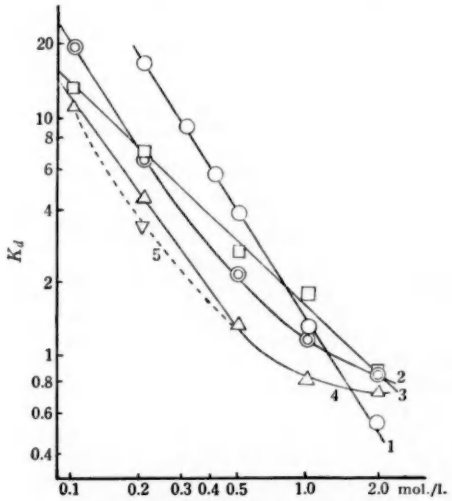

Fig. 1. Relationship between K_d and the concentration of nitrate ions in eluants.
1: Sodium thiosulfate. 2: Sodium sulfate. 3: Sodium sulfide. 4: Sodium sulfite by neutral eluant. 5: Sodium sulfite by an alkaline eluant of pH≒9.7.

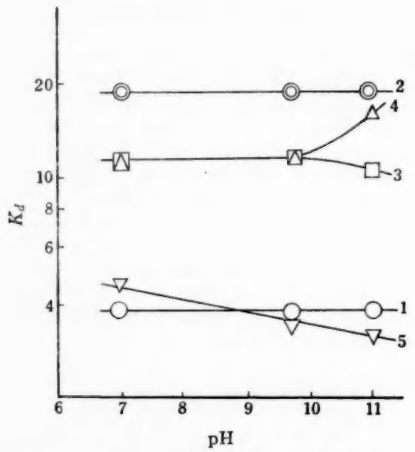

Fig. 2. Relationship between K_d and the pH of eluant.
1: Sodium thiosulfate eluted by 0.5 mol./l. nitrate solution. 2: sodium sulfate eluted by 0.1 mol./l. nitrate solution. 3: sodium sulfide eluted by 0.1 mol./l. nitrate solution. 4: Sodium sulfite eluted by 0.1 mol./l. nitrate solution. 5: Sodium sulfite eluted by 0.2 mol./l. nitrate solution.

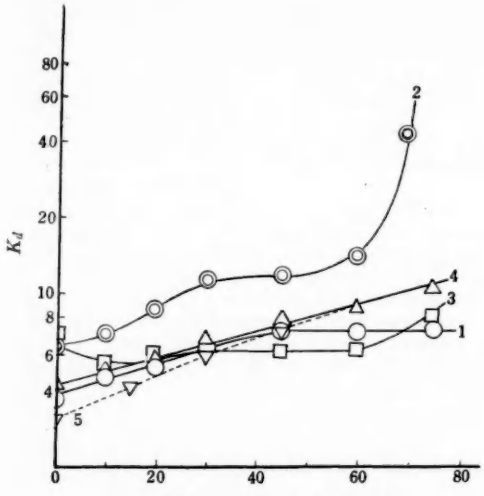

Fig. 4A. Relationship between K_d and the volume percentage of organic solvent in eluant.
1: Sodium thiosulfate. 2: Sodium sulfate. 3: Sodium sulfide. 4: Sodium sulfite eluted by neutral eluant. 5: Sodium sulfite eluted by alkaline eluant of pH≒9.7. The concentration of nitrate ion used as the eluant was 0.5 mol./l. for thiosulfate, and 0.2 mol./l. for the other salts.

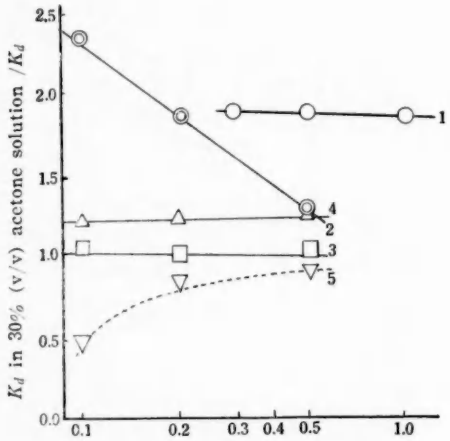

Fig. 3. Relationship between K_d in 30% (v/v) acetone solution /K_d in aqueous solution and the concentration of nitrate ion in eluant.
1: Sodium thiosulfate. 2: Sodium sulfate. 3: Sodium sulfide. 4: Sodium sulfite eluted by neutral eluant 5: Sodium sulfite eluted by alkaline eluant of pH≒9.7.

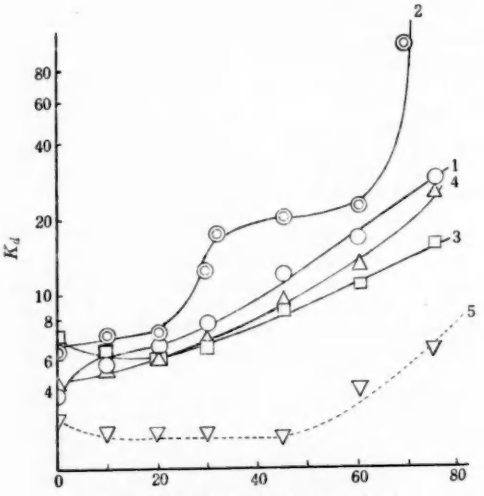

Fig. 4B. Relationship between K*d* and the volume percentage of organic solvent in eluant. The same legend as Fig. 4A. stands for Fig. 4B.

mixing ammonium nitrate, sodium nitrate and ammonia, was used. The pH was checked by a glass electrode pH meter (Type 43, made by Iio Denki Co.). The results are shown in Fig. 2. There is no remarkable change of K_d in this pH region, though the K_d of sulfite and sulfide eluted with 0.1 mol./l. nitrate solution showed a slight deviation with increase in pH at about pH 9~11.

The Effect of Organic Solvent on the Distribution Coefficient.—When the eluant which contained 30% (by volume) of acetone was employed together with various quantities of nitrate in place of aqueous solution, the value of the distribution coefficient showed deviation. The relation between the ratio of the K_d values thus determined in 30% (by volume) acetone solution to the K_d values of the original aqueous solution of the nitrate ion and the concentration of eluant was shown in Fig. 3. In the case of sulfide, the K_d in 30% (by volume) acetone solution is not affected by the addition of acetone, while the K_d values of thiosulfate and sulfite in 30% (by volume) acetone solution become 1.9 and 1.1 times greater than the values of K_d determined in the original aqueous solution, respectively. The concentration of nitrate does not affect the ratio K_d in 30% (by volume) acetone solution and that in aqueous solution. In the case of sulfate, this ratio increased with the decrease of the concentration of nitrate. Generally the increase of K_d in 30% acetone solution by the addition of organic solvent may be caused by the stripping off of the hydrated water molecules surrounding the anion of oxy-acid of sulfur. In the case of sulfite in alkaline solution, however, a decrease of K_d was recognized in 30% acetone solution.

In the next place, in order to clarify the effect of organic solvent on the adsorbability of these anions, the relationship between K_d and concentration of ethanol or acetone was examined, the concentration of nitrate being kept constant (0.5 mol./l. for thiosulfate and 0.2 mol./l. for other anions). The results were shown in Figs. 4A and 4B.

Experimental results showed a remarkakle increase of K_d values with the percentage of organic solvent. In general, the increase of K_d values by the addition of acetone is greater than that by the addition of the same percentage of ethanol. But exceptions were recognized in cases of sulfite by acetone, and of sulfide by ethanol. In these cases the K_d values decrease until they reach constant in spite of the increase in amount of organic solvent (even up to 40~60% by volume). From this result, the method of separation of sulfite, sulfide and sulfate is suggested, that is, the use of eluant which contains 30% (by volume) of actone and 0.1 mol./l. of nitrate, with pH adjusted to 9.7 by ammonia.

In addition to these measurements of K_d values using Diaion SA #100, the measurements by the use of Amberlite IRA-410 were also carried out. But the K_d values for the latter resin almost exactly coincided with those for the former resin within the range of experimental error.

Discussion on the Variation of Distribution Coefficients.—Judging from the slopes of the curves shown in Figs. 1 and 2, sulfate and thiosulfate may exist in the form of doubly charged anion, and their adsorbability does not change in the range of pH 7~11. The effect of organic solvent upon thiosulfate and sulfate is shown in Figs. 4A and 4B. In these data, an inflexion point is recognized at about 10% (by volume) in acetone for thiosulfate and at about 30% for sulfate. These facts may be attributed to some discontinuous dehydration grade of these anions. In the case of sulfide, as is shown in Fig. 1, the HS^- ion may be a predominant species as is expected from the slope of the curve. The effect of adding ethanol, as is shown in Fig. 4A, keeps the K_d constant even up to 60%, while the increase of K_d by acetone appeared even at 30%. These phenomena may be caused by a special interaction between ethanol and sulfide, ions. In the case of sulfite, the formation of a compound between sulfite ions and acetone is expected,[4] whereas, as is shown in Figs. 4A and 4B, the K_d in a neutral solution shows no special change compared with the other oxy-acid ions; in other words, only a monotonous increase of K_d with the increase of the content of organic solvent was observed. But, in the case of alkaline solution, the K_d decreases and then remains constant even up to 45% of acetone. This fact can perhaps be ascribed to the formation of special compounds between acetone and sulfite or between acetone, ammonia

4) G. Gabrielson and O. Samuelon, *Svensk. Kem. Tid.*, **62**, 214 (1950).

TABLE I

THE ANALYSIS OF MIXED SAMPLES OF SULFITE, SULFATE, AND THIOSULFATE

		Sulfite	Sulfate	Thiosulfate
Added.	mg.	6.39	19.4	20.0
Observed.	mg.	6.32±0.064	19.0±0.41	20.0±0.20
	%	99.0±1.0	98.0±2.0	100.0±1.0

TABLE II

THE ANALYSIS OF MIXED SAMPLE OF SULFITE, SULFATE, SULFIDE AND THIOSULFATE

		Sulfite	Sulfide	Sulfate	Thiosulfate
Added	mg.	7.00	2.96	19.3	21.98
Observed.	mg.	6.93±0.69	2.78±0.16	18.58±0.30	22.20±0.22
	%	99.0±1.0	94.1 ±5.5	96.3 ±1.5	101.1 ±1.0

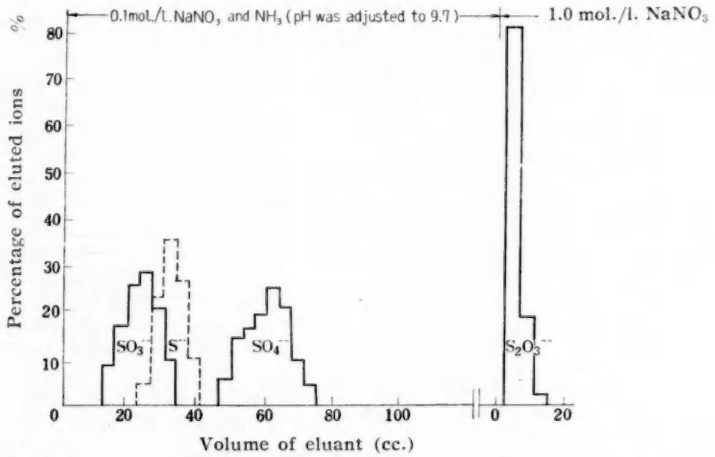

Fig. 5A. Elution curve of a mixed sample. The flow rate was 0.3 cc./min.

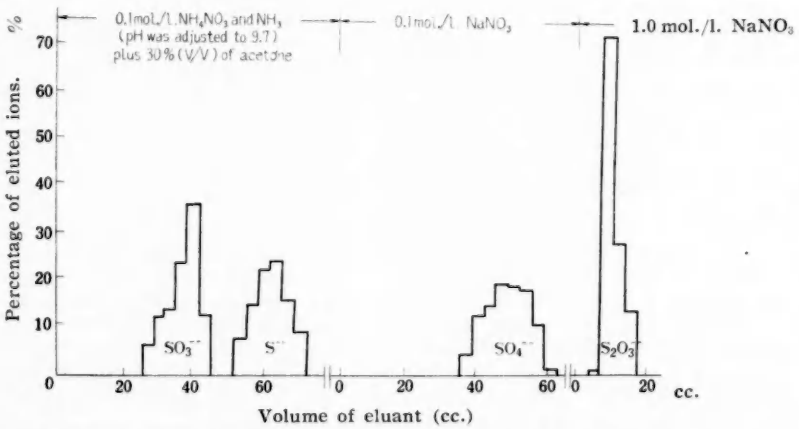

Fig. 5B. Elution curve of a mixed sample. The flow rate was 0.1 cc./min.

and sulfite[5]. In alkaline solution without acetone the K_d of the sulfite ion shows only slight deviation from the K_d of sulfite ion in a neutral solution as shown in Fig. 1, from which it is inferred that this phenomenon is due neither to the change in the form of the sulfite ion only, nor to the reaction between the ammonia and the sulfite ion before the addition of acetone.

The Chromatographic Separation of Sulfate, Sulfite and Thiosulfate.—When sulfide does not coexist with the other three, the result shown in Fig. 1 may be applicable to their separation. By using 0.1 mol./l. of nitrate solution, first sulfite, and next sulfate were eluted; then thiosulfate was eluted by 1.0 mol./l. of nitrate solution. But, when the neutral nitrate solution was used as an eluant, recovery of sulfite did not reach 100%, and accordingly it was necessary to use an alkaline eluant. The 0.1 mol./l. ammonium nitrate solution with the pH adjusted to 9.7 by ammonia was most suitable. The ion-exchange resin Diaion SA ♯100 of analytical grade mounted in a column of 0.7 cm. in diameter and 17 cm. in length was employed. The amount of the resin used was 4.9 g. The results are shown in Fig. 5A. The collected sulfite and thiosulfate were titrated with the standard solution of iodine, while the quantity of sulfate was determined gravimetrically in the form of barium sulfate.

The analysis by this method is simpler than the method which is shown in the next paragraph, because the flow rate is kept relatively great and the quantity of sulfite is determined by titration.

The recovery percentage of oxy-acid ions of the known composition shown in Table I was calculated from the data of the experiments repeated five times.

The Chromatographic Separation of Sulfate, Thiosulfate, Sulfite and Sulfide.—When sulfide is present, sulfide and sulfite are not separable by an elution with simple nitrate solution. The nitrate solution containing acetone can be employed for this purpose, as was expected from the data shown in Fig. 4B. The resin column is the same as that used in the experiment shown in Fig. 5A.

Sulfite and sulfide are first eluted successively by the eluant containing 30% (by volume) of acetone, 0.1 mol./l. of ammonium nitrate, with its pH adjusted to 9.7 by ammonia; second, sulfate is eluted with 0.1 mol./l. sodium nitrate, and finally thiosulfate by 1.0 mol./l. sodium nitrate. A typical run of such experiments is illustrated in Fig. 5B.

The quantity of collected sulfite is determined gravimetrically in the form of barium sulfate after oxidation by sodium peroxide in alkaline solution. Sulfide is titrated by standard iodine solution.

A example of recovery of each salt by this method, with the percentage calculated from the experiments repeated twelve times is shown in Table II.

From the results of these experiments it was found that this method can be used for the analysis of these salts. In the results shown in Table II, however, the recovery of sulfide is slightly less than the theoretical value. This defect may be remedied by improving the acceptor of the effluent so as to protect hydrogen sulfide from escaping.

Summary

1. The distribution coefficients of sulfate, thiosulfate, sulfite and sulfide in the nitrate solution were measured.

2. By the addition of ethanol or acetone to the neutral eluant solution, the adsorbability of sulfate, sulfite, thiosulfate and sulfide was increased, while that of sulfite in alkaline acetone solution showed a marked decrease.

3. By the use of these results a mutual separation of sulfate, thiosulfate, sulfite and sulfide was effected by the anion-exchange chromatography.

The author desires to express his gratitude to Professor T. Shirai, Dr. Y. Yoshino and to his colleagues in the laboratory for their suggestions and for the discussion helpful in publishing this paper.

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5) For example, G. Palmer, "Experimental Inorganic Chemistry" Cambridge Univ. Press, England, p. 330 (1954).

*On the Determination of Fine Structure of Cellulosic Fibers**

By Taketoshi KŌSHIRO, Kazuo YAGAMI, Eiichiro SHIRATSUCHI and Toshikazu FUJIMURA

(Received October 7, 1957)

It is well known that the mechanical properties of cellulosic fibers depend on their fine structure. P. H. Herrent and A. Lude suggested double net-work structure, in which the crystalline regions constitute the knots[1]. Therefore, it seems significant to clarify the nature of crystalline regions. The mean crystallinity determined by existing methods is insufficient to elucidate the mechanical properties, then it is desirable to estimate the distribution of order and of size. W. A. Sisson and J. A. Howsmon have proposed "lateral order" $\bar{O}$ which was defined by the equation,

$$\bar{O} = (OH)_c/(OH)_t$$

Where $(OH)_c$ is the total number of hydrogen bonds in the region and $(OH)_t$ is the total possible number of hydrogen bonds if all the molecules are perfectly crystallized. This value is dependent on the choice of the volume element. If this volume is too large, the curves as depicted become single sharp peak at $\bar{O}$ corresponding to an average order; if too small, the curves split into two sharp peaks at zero order and perfect order[2]. To measure the lateral order distribution, Maeda and Yurugi applied fractional solution of hydrolyzed cellulose[3] and the methods which determine the moisture regain or levelling-off degree of polymerization after mercerization, were suggested[4]. These methods are based on the thermodynamic properties and do not have direct relation to the fine structure.

Recently, the distribution of crystallite sizes is estimated by means of X-ray diffraction[5] or electron microscopy[6].

In the present paper, on the assumption that the length of crystalline residue corresponds to the length of hydrogen-bond train along cellulose molecule chain, we have undertaken to determine its distribution by the molecular weight fractionation of the residue which is freed from the amorphous region by hydrolysis or its modification. Since recrystallization has been found to occur during acid hydrolysis[7,8], the following methods were tried to avoid it.

(1) Ordinary aqueous acid hydrolysis after partial acetylation or partial oxidation with lead tetra-acetate, which may prevent the recrystallization by steric hindrance due to the modification in amorphous region.

(2) Methanolysis, which is carried out in non-aqueous medium to prevent additional forming of hydrogen-bond.

(3) Oxidizing hydrolysis with sulfuric acid containing potassium dichromate. It is effective in removing the amorphous chain ends produced by chain cleavage, before recrystallization takes place. The residues after these treatments were nitrated and fractionated, and the chain length distribution curves were obtained. The availability of these methods and the fine structure of rayon staple were discussed.

Experimental

Materials. Commercial viscose rayon staple (Bright regular 1.5 D) was steeped in water and then the water was replaced with reaction medium.

Methods. *a) Apparent total crystallinity.*—It was given as a weight per-cent yield of the residue after the hydrolysis or its modified treatments.

b) Average degree of polymerization ($\overline{DP}$).—It was determined from the viscosity of cuprammonium solutions, or that of acetone solution of

* Presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1957.

1) P. H. Herrent and A. Lude, *Textiel Research J.*, **21**, 137 (1951).

2) Otto-Spurlin "Cellulose and Cellulose Derivatives", Interscience Publishers, New York, Vol. I, (1954) p. 252.

3) H. Maeda, *J. Soc. Textile Cellulose Ind. (Japan), (Sen-i Gakkaishi)* **12**, 6 (1956); T. Yurugi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kōgyō Kagaku Zassi)* **58**, 27 (1955).

4) L. Jörgensen, *Acta Chem. Scand.*, **3**, 790 (1949); **4**, 185, 658 (1950); O. A. Battista et al. *Ind. Eng. Chem.*, **48**, 333 (1956).

5) K. Kobayashi, presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1957.

6) E. A. Immergut and B. G. Rånby, *Ind. Eng. Chem.*, **48**, 1183 (1956).

7) H. Mark, F. C. Brenner and V. Frilette, *J. Am. Chem. Soc.*, **70**, 877 (1948).

8) P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 315 (1949).

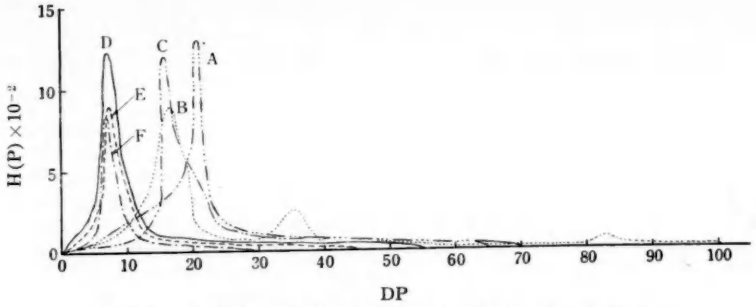

Fig. 1. Chain-length distribution of hydrolyzed cellulose.

A	Maeda's method	D	4 N HCl 1 hr.
B	1 N HCl 1/6 hr.	E	4 N HCl 4 hr.
C	1 N HCl 1 hr.	F	4 N HCl 6 hr.

the nitratde products. An Ostwald viscometer was employed and the intrinsic viscosity was calculated by Schulz-Blaschke's Formula.

c) ***Chain-length distribution.***—The sample was nitrated with Mitchel's mixed acid[9] and dissolved in acetone and fractionated using water as the precipitant.

d) ***Accessibility.***—Iodine sorption method of Hessler and Power[10] was employed. Concentration of sodium sulfate was 200 g./l. and the sorption was carried out at 20±0.1°C for an hour.

e) ***Partial acetylation pretreatment.***—The rayon staple swollen with glacial acetic acid was treated at 50°C for twelve hours with the mixture, which consists of 6 volumes pyridine, 8 volumes acetic acid and 60 volumes benzene.

f) ***Partial oxidation pretreatment.***—The samples swollen with glacial acetic acid were treated at 50°C for twenty hours with the glacial acetic acid solution which contains 0.077 M lead tetra-acetate. The lead tetra-acetate used was prepared according to Colson's method[11].

g) ***Hydrolysis.***—Samples were refluxed at 100°C with hydrolyzing agents. After the pre-determined reaction time, the residue was filtered off with a glass filter and washed with water to neutral. Then its moisture was exchanged with absolute alcohol, and it was dried in vacuo at 50°C for five hours and weighed.

h) ***Methanolysis.***—Samples were first refluxed at 68°C with methanol, saturated with dry hydrogen chloride gas, and then the residue was washed to neutral with absolute alcohol and dried in vacuo.

i) ***Oxidizing-hydrolysis.***—A similar procedure to hydrolysis was used except that the hydrolyzing mixture, consisted of 1 N sulfuric acid and 0.017 M potassium dichromate.

Results

A) Ordinary Acid Hydrolysis. — The effects of acidity, reaction time and substrate on the yield and the $\overline{DP}$ of the residue are shown in Table I. The levelling-off degree of polymerization (LODP) of these samples was obtained by the treatment with 1 N hydrochloric acid for an hour.

TABLE I

DEGREE OF POLIMERIZATION AND YIELD OF RESIDUE AFTER ORDINARY HYDROLYSIS

Conditions of Hydrolysis			Residue	
Acidity of HCl N (aq.)	Temp. °C	Time hr.	Yield wt. %	$\overline{DP}$ (Nitrate)
1	100	1/6	98.8	26
		1	90.0	22
4	100	1	72.4	22
		2	57.5	22
		4	43.9	22
		6	37.0	22
Maeda's Method*	80	6	98.1	23

* Mixture of 5 parts 3.5 N HCl and 95 parts ethanol.

As shown in Fig. 1, the peak of distribution curve shifts to lower DP regions with the increase of acidity or reaction time, but after the peak has attained a definite DP, only the height of the peak decreases.

TABLE II

DEGREE OF POLIMERIZATION AND YIELD OF HYDROLYZED RESIDUE AFTER PRETREATMENT

(Conditions of Hydrolysis: 1 N HCl, 100°C, 25 hr.)

Pretreatment method	Degree of Substitution (M/C_6 unit)	Residue	
		Yield wt. %	$\overline{DP}$ (Cupram.)
Acetylation	0.331	58.8	17.5
Oxidation	0.157	25.2	
No Treatment	0	65.5	25.4

9) R. L. Mitchel, *Ind. Eng. Chem.*, **38**, 843 (1946).
10) L. E. Hessler and R. E. Power, *Textile Research J.*, **24**, 822 (1954).
11) A. Colson, *Compt. rend.*, **136**, 1, 676, 892 (1903).

B) Effect of Pretreatment. — The weight loss and $\overline{DP}$ of the hydrolyzed residue after pretreatment are shown in Table II. Generally speaking, pretreatments caused severe degradation. The chain length distributions of the above residues are shown in Fig. 2.

C) Methanolysis.—The effects of acidity in methanolysis are shown in Table III. The reaction is accelerated by the increase of acidity and the yield of residue decreases. However, little decrease in LODP and accessibility was observed.

The reaction rate of methanolysis is retarded by the addition of water, and the yield and the $\overline{DP}$ of the residue decreases with the increase in water content. Hydrochloric acid in the reagent is consumed very rapidly in the absence of water, but little at 100% aqueous medium, as shown in Fig. 3. The methanolysis gives higher ultimate yields of residue than the hydrolysis, although methanolysis proceeds initially at higher rates.

The results of fractional solution in which caustic soda solutions up to 8% are used as solvents and by which the residual amorphous portions may be dissolved owing to the probable imperfect removal, are shown in Fig. 4. Fig. 5 gives the chain-length distribution of methanolyzed

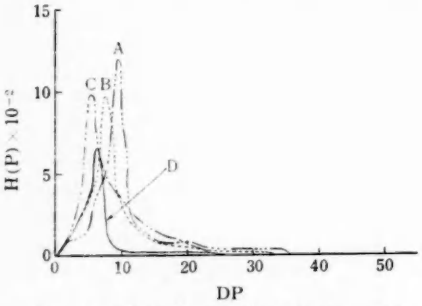

Fig. 2. Chain-length distribution of hydrolyzed cellulose after pretreatment.

Pretreatment		Hydrolysis: Acidity of HCl	Hydrolysis: Time hr.
A	None	1 N	25
B	None	4 N	2
C	Acetylation	1 N	25
D	Oxidation	1 N	25

TABLE III

DEGREE OF POLYMERIZATION, ACCESSIBILITY AND YIELD OF RESIDUE AFTER METHANOLYSIS

(Temp. of Methanolysis, 67±1°C)

Condition: Acidity N	Condition: Time hr.	Residue: Yield wt. %	Residue: $\overline{DP}$ (Cupram.)	Residue: Accessibility %
2.5	0	100.0	293.5	
	1/3	93.0		
	1	90.0		33.9
	3	87.0	30.0	
	8	83.5	27.9	25.8
	24	78.9	27.0	24.3
4	2	75.6	30.6	28.2
	6	74.7	28.4	25.3
	12	73.0	26.2	24.8
6	2	71.7	29.0	23.6
	6	67.7	27.4	24.3
	12	64.6	26.2	22.9
8	12	58.3	26.2	19.5

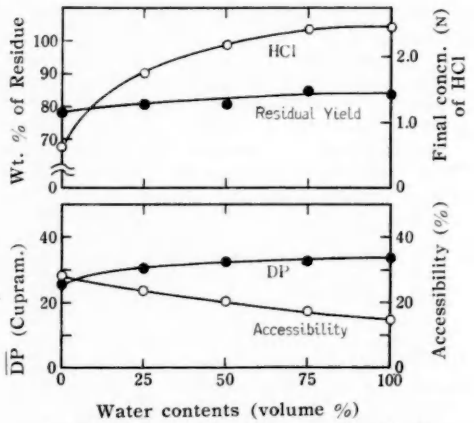

Fig. 3. Effects of water in methanolysis reagent. Methanolysis, 2.5 N HCl, at 68°C, 24 hr.

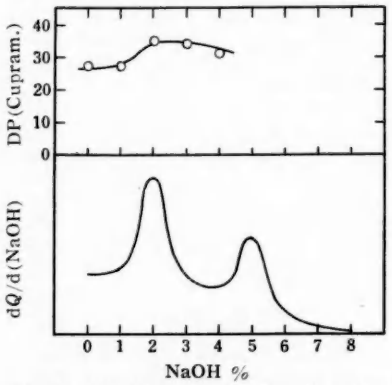

Fig. 4. Alkali extraction of methanolyzed cellulose. Methanolysis 1 N HCl, 68°C, 24 hrs. alkali extraction 20°C, 1 hr.
Q: weight loss of alkali extraction.

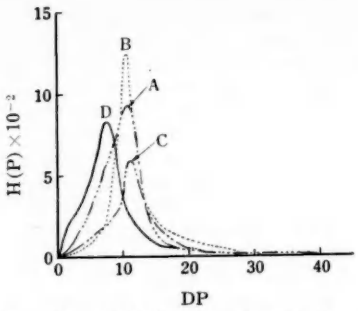

Fig. 5. Chain-length distribution of methanolyzed, and its alkali-extracted cellulose.
A ——— 2.5 N HCl in MeOH 24 hr.
B ····· 2% alkali-extracted residue of A.
C —·—· 4% alkali-extracted residue of A.
D ——— 8 N HCl in MeOH 12 hr.

TABLE IV
DEGREE OF POLYMERIZATION, ACCESSIBILITY AND YIELD OF RESIDUE AFTER OXIDIZING-HYDROLYSIS
(Conditions of solvolysis: 100°C, 0.017 M $K_2Cr_2O_7$, 1 N H_2SO_4)

Reaction Time hr.	Residue Yield wt. %	$\overline{DP}$ (Cupram.)	Accessibility %
0	100.0	293.5	51.8
1	73.1	27.7	11.8
3	65.7	26.5	11.6
5	61.5	24.6	11.5
8	59.0	24.4	11.4
12	57.0	23.9	11.4

residue and its alkali-extracted residue.

D) Oxidizing-Hydrolysis. — Samples were oxidized and simultaneously hydrolyzed with the mixture of potassium dichromate and sulfuric acid, and the effect of the reaction time on the yield, DP and the accessibility of the residue are shown in Table IV.

It is very characteristic that the accessibility of the residue obtained from the oxidizing hydrolysis, levels off rapidly and exhibits relatively lower values than those of the other degradation residues.

The residue from the oxidizing hydrolysis is wholly dispersed in 2% caustic soda solution. Fig. 6 gives the chain-length distribution of this residue at various reaction times.

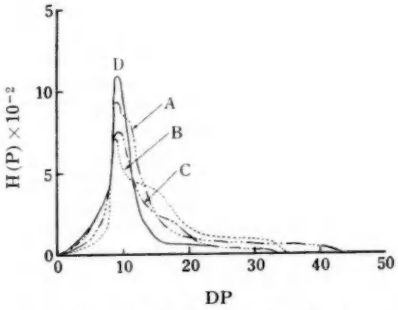

Fig. 6. Chain-length distribution of oxidizing-hydrolyzed cellulose.
A ——— 0.017 M $K_2Cr_2O_7$ + 1 N H_2SO_4 3 hrs.
B ····· 〃 〃 5 hrs.
C —·—· 〃 〃 8 hrs.
D ——— 〃 〃 12 hrs.

Discussion

Ordinary Hydrolysis Process. — The results that the peak of chain-length distribution curves of hydrolyzed residue moves initially to lower DP as the hydrolysis proceeds and then after it has attained a definite limit, only the height of the peak decreases, is in agreement with the observation by electronmicroscope that during the hydrolysis process the distribution of crystalline length remains almost constant and the distribution of crystalline width shifts to a more narrow side[6].

TABLE V
COMPARISON OF VARIOUS METHODS

Method	Conditions Concn.	Time hr.	Residue Yield wt. %	Accessibility %	$\overline{DP}$	Mode of DP
Ordinary hydrolysis	4 N	2	52.9	12.6	29	7
Hydrolysis after acetylation	1 N	25	58.5			6
Hydrolysis after oxidation	1 N	25	25.2			7
Oxidizing-hydrolysis	0.017 M + 1 N	8	61.8	11.4	24	9.5
Methanolysis	8 N	12	58.3	19.5	26	7.5
Alkali extraction after methanolysis	4% + 2.5 N	24	31.3	14.0	31	12

Comparison of Various Methods for Removal of the Amorphous Region.—The results of various methods are summarized in Table. V.

In the case of the methanolysis with 8 N hydrochloric acid, the peak of chain-length distribution is located at a somewhat lower DP. However, its residue which is controlled to give similar yield to other methods, exhibits high levelling-off accessibility, high partial solubility in 4% caustic soda solution and somewhat higher DP. These results suggest that the methanolyzed cellulose contains considerable amorphous regions. In our experiment with methanol-water systems, the yield of residue and its DP increase, and its accessibility decreases with the increase in water content. From these results, it may be concluded that water increases the probability of recrystallization and methanol has the reverse effect. However, Nelson et al. have described recently that the methanolysis prevented the reversion of cellulose III to cellulose I but appeared not to avoid the recrystallization[12]. Therefore, methanolysis or hydrolysis is not suitable for our object.

The chain-length distribution of hydrolyzed residue seems to shift its peak to lower DP regions on oxidation pretreatments. Therefore, the pretreatment may hinder the growth of the crystallites, but the low yield may be derived from the destruction of the crystallite, especially by the severe action of lead tetra-acetate. The chain-length distribution of the hydrolyzed residue from acetylation pretreatment has a similar width of DP range, but its peak exists at a slightly lower DP, compared with ordinary hydrolysis. The degree and the distribution of degradation may be influenced by the heterogeneity of the acetylation pretreatment. From the above reason and the troublesome operation which requires a long time, pretreatment methods are not so desirable.

In order to remove the amorphous region which remains around the end of the crystallites during hydrolysis, the oxidizing-hydrolysis method was carried out with dichromic acid whch is considered not likely to penetrate into the crystalline region. The results that the peak of chain-length distribution shifts to slightly higher DP, but the shoulder on the higher DP side disappears and the DP decrease, seem to disprove the recrystallization. Since oxidizing-hydrolysis gives lower levelling-off accessibility than ordinary hydrolysis, the residue of oxidizing-hydrolysis may show probably the original crystalline state. However, since its residue is easily soluble in dilute alkaline solution, the carboxyl groups formed by the oxidation may be responsible for its solubility in alkaline solution and for the poorer iodine sorption which results apparently in lower accessibility.

Although further study by means of X-ray diffraction, infrared absorption analysis etc. is necessary, oxidizing-hydrolysis may be the most hopeful.

Fine Structure of Rayon Staple.—From the above results, it is estimated that the length of crystalline region distributes within the range up to approximately the DP of 40 (ca. 200 Å) and its distribution has one peak between 6 and 10.

Relation between the Lateral Order and the Chain-Length Distribution of Solvolyzed Residue.—Maeda determined "lateral order", based on the solubility of hydrolyzed residue in alkaline solution, C, which is given by the following equation,

$$C = A \exp(-PE/RT)$$

where P is the degree of polymerization, E transition energy of solution per glucose unit, R gas constant, T absolute temperature, because E can be substituted for "lateral order"[13]. However, even an intensively degraded sample has so wide a chain-length distribution that the solubility in alkaline solution would depend not only on E, but also on P, as the lower DP region of methanolyzed residue is more soluble in alkaline solution.

If the chain-length of suitably degraded residue coincides with the length of the crystallite formed by hydrogen bond without gap, this length may indicate the fine structure of cellulosic fiber more clearly than the so-called "lateral order", which depends theoretically on the volume in consideration. But the solubility of the methanolyzed residue or the residue from the oxidizing hydrolysis in alkaline solution suggests the possibility of cracks in hydrogen-bonded crystallite.

Summary

In order to clarify the fine structure of

12) M. L. Nelson, L. Segal, T. Mares and J. J. Creely, *J. Polymer Sci.*, **20**, 29 (1956).

13) H. Maeda, *J. Soc. Textile Cellulose Ind. Japan, (Sen-i Gakkaishi)* **12**, 6 (1956).

rayon staple, it may be necessary to estimate not only the total crystallinity but also the distribution of crystalline size and quality. For this purpose, various methods which seemed to remove the amorphous region without recrystallization, were studied.

Methanolysis is affected by water content in the mixture and its residue may still contain an amorphous region because of its high accessibility. The recrystallization may be possible during not only hydrolysis but also methanolysis.

The hydrolysis after pretreatment is not very effective to prevent recrystallization and may destroy crystalline region. Moreover, its procedure is troublesome.

The oxidizing-hydrolysis, which shifts the crystalline length distribution toward slightly higher DP region diminishing the shoulder on higher DP side and gives the lowest levelling-off accessibility, holds out considerable promise for the elucidation of the original crystalline structure. But its high solubility in alkaline solution may be derived from a carboxyl group formed during oxidation or from the cracks in a hydrogen-bond train of crystallites. Therefore, problems to study still remain.

The crystalline region of viscose rayon staple seems to have the chain-length distribution, which extends to a DP of ca. 40 and shows one maximum between the DP of 6 and 10.

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Crystal Structure of Quinhydrone, $C_{12}H_{10}O_4$

By Haruo MATSUDA,* Kenji OSAKI and Isamu NITTA

(Received March 17, 1958)

The peculiar properties of some aromatic molecular compounds and the question as to the forces responsible for their formation have been attracting the attention of a number of authors. Anderson[1] investigated a series of molecular compounds containing quinone, or its derivatives, and concluded that in all these compounds the component molecules are alternately stacked plane to plane, and that the most probable mechanism for the binding is effected by the interaction between strongly polar groups and by the highly anisotropic and polarizable aromatic systems. Such a type of parallel stacking was also found in *p*-iodoaniline-*s*-trinitrobenzene[2] which was the first example fully analyzed among the aromatic molecular compounds. For the discussion of the nature of intermolecular attraction, however, it is very desirable to obtain more data on inter- and intra-molecular distances and bond angles in these aromatic molecular compounds.**

Quinhydrone, or benzoquinhydrone, is the simplest of the series of molecular compounds containing quinones. It is highly desirable to determine its structure in detail, though there have been published a few papers which describe the general arrangement of molecules in this crystal.

Palacios and Foz reported in their first paper[3] that the monoclinic unit cell ($\beta = 90°$) of quinhydrone contains one formula unit $C_{12}H_{10}O_4$ and the molecules are linked in endless chains by symmetrical hydrogen bonding. This structure in which both the molecules of quinone and hydroquinone are placed in the same equivalent positions, so that they are not distinguishable, was however revised by the same authors[4].

* Deceased 1960. This work, especially the most laborious part of it, was almost completed by H. Matsuda. It was continued and written up after his death.

1) J. S. Anderson, *Nature*, **140**, 583 (1937).

2) H. M. Powell, G. Huse and P. W. Cooke, *J. Chem. Soc.*, **1943**, 153.

** When the present work was almost completed, Dr. Wallwork was so kind as to inform us of his detailed analysis of phenoquinone. See S. C. Wallwork and T. T. Harding, *Nature*, **171**, 40; T. T. Harding and S. C. Wallwork, *Acta Cryst.*, **6**, 791 (1953); **8**, 787 (1955).

3) O. R. Foz and J. Palacios, *Anales Soc. Españ. Fis. Quim.*, **30**, 421 (1932).

4) J. Palacios and O. R. Foz., *Anales Soc. Españ. Fis. Quim.*, **33**, 627 (1935); **34**, 773 (1936).

They observed weak superstructure reflections requiring doubled a and c axes, and they ascribed the observed subperiodicity to the discrete existence of quinoid and quinoloid units in the structure. This view is in accord with that of Anderson quoted above.[1]

Preliminary Investigations.—Most of the well-defined, apparently single crystals grown from acetone solutions have the appearance of hexagonal prisms. Laue photographs showed, however, that they are twins, and that the axial angle β was not exactly equal to 90° as has been reported. The deviation was estimated from the separation of Laue spots to be about 45′. Single crystals were easily obtained by splitting these twins with the aid of a razor blade and were used for subsequent works.

Lattice constants, derived from a series of symmetrical back reflection photographs, are

$$a=7.674\pm0.001\text{Å}, \quad b=6.001\pm0.001\text{Å}$$
$$c=21.788\pm0.002\text{Å}, \quad \beta=90°38'\pm3'.$$

Four $C_{12}H_{10}O_4$ units are contained in this lattice and the calculated density is 1.444 g./cm^3 as compared with the observed value 1.401 at 20°C. Systematic extinctions were observed in (hkl) when $h+l$ is odd, in $(0k0)$ when k is odd and in $(h0l)$ when $h-l$ is not multiple of 4. The only space group which conforms to these rules is $C_{2h}^5-B2_1/d$ with the glide translation $(a-c)/4$ for the above set of axes. The symmetry elements of this space group are shown in Fig. 1, and general and special point positions are listed in Table I. This lattice can be reduced to another having $a=7.647$ Å, $b=6.001$ Å, $c'=11.590$ Å and $\beta'=109°58'$ expressed in terms of $P2_1/c$, if we take the c'-axis as indicated in Fig. 1. Although this expression is more common, the former one ($\beta\approx90°$) was adopted throughout this work for the sake of convenience.

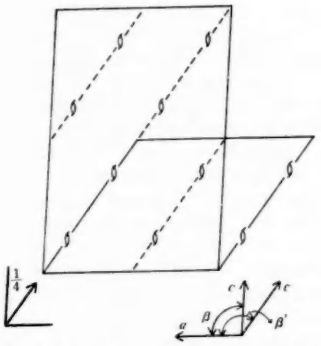

Fig. 1. Unit cell and symmetry elements of $B2_1/d$ and its reduction to $P2_1/c$.

Determination of the Averaged Structure.—A characteristic feature of the X-ray pattern of quinhydrone, as has been reported by Palacios and Foz, is that all the reflections with h, l odd are very weak, compared with those with h, l even. If we construct a Fourier representation of such a structure using even reflections alone, we shall obtain a hypothetical averaged structure repeating with lattice dimensions $(1/2)\,a$, b and $(1/2)\,c$. This averaged structure will be a fairly good approximation to the "true" structure, since reflections with h, l odd are all weak and will not contribute much to the Fourier representation of the true structure. Therefore first we determined this averaged structure and then proceeded to the true one.

The hypothetical averaged structure introduced above contains only one sort

TABLE I

GENERAL AND SPECIAL POINT POSITIONS FOR THE ADOPTED SPACE GROUP $B2_1/d$

8-fold general positions

$$8\ (e):\ \pm\left[\begin{array}{lll} x,\ y,\ z & ; & \frac{1}{2}+x,\ y,\ \frac{1}{2}+z \\ \frac{1}{4}+x,\ \frac{1}{2}-y,\ \frac{3}{4}+z & ; & \frac{3}{4}+x,\ \frac{1}{2}-y,\ \frac{1}{4}+z. \end{array}\right]$$

4-fold symmetry centers

$$4\ (a):\ 0\,0\,0,\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{4}\tfrac{1}{2}\tfrac{3}{4},\ \tfrac{3}{4}\tfrac{1}{2}\tfrac{1}{4}. \quad (H)$$

$$4\ (b):\ \tfrac{1}{2}0\,0,\ 0\,0\tfrac{1}{2},\ \tfrac{1}{4}\tfrac{1}{2}\tfrac{1}{4},\ \tfrac{3}{4}\tfrac{1}{2}\tfrac{3}{4}. \quad (Q)$$

$$4\ (c):\ 0\tfrac{1}{2}0,\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{4}0\tfrac{3}{4},\ \tfrac{3}{4}0\tfrac{1}{4}.$$

$$4\ (d):\ \tfrac{1}{2}\tfrac{1}{2}0,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{4}0\tfrac{1}{4},\ \tfrac{3}{4}0\tfrac{3}{4}.$$

of averaged molecule $1/2(C_{12}H_{10}O_4)$ lying on two of the centers of symmetry in a lattice of space group $P2_1/n$, and corresponds to the structure given in the first paper of Foz and and Palacios.[3] The

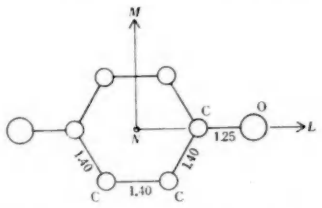

Fig. 2. Molecular model used in calculating the Fourier transform. The weight of the oxygen atom was taken to be 4/3 times that of the carbon. Axis N points up and is perpendicular to both L and M.

orientation of the molecular axes was determined easily by the method of Fourier transform[5] using the reflections $(0k0)$ and $(00l)$. In calculating this transform, a hypothetical molecular model shown in Fig. 2 was adopted. Atomic parameters thus obtained were refined through repeated $\rho(yz)$ syntheses and structure-factor calculations $(0kl)$.

The averaged structure obtained here was in striking accordance with that suggested by Banerjee[6] from magnetic data. According to our results, the normal to the averaged molecular plane, when projected upon (010), makes an angle 15.0° with the a axis, which accords well with the angle 15.1° between the a axis and the direction of maximum susceptibility reported by Banerjee. This fact alone will support Banerjee's view that the crystal of quinhydrone consists of molecules of quinone and hydroquinone.

Determination of x and z Parameters. —Since there are four $C_{12}H_{10}O_4$ units in the unit cell having eight-fold general positions, two types of structure are possible; one of which consists of two different kinds of molecules, corresponding to quinone and hydroquinone, each lying on one of the four-fold centers of symmetry, say 4(a) and 4(b) (Table I.); and the other consists of only one kind of molecule (semiquinone type) which are situated around (1/4 0 0), etc. Since the former type consisting of quinone and hydroquinone seemed to be more plausible in view of the work of Anderson[1] and that of Banerjee[6], we studied mainly on this line. We also examined the semiquinone type structure, which we shall later mention briefly.

In order to find out how and to what extent these two sorts of component molecule deviate in shape and orientation from the hypothetical averaged molecule, we performed trial-and-error calculations on $(h0l)$ reflections with h and l odd, using scaled structure factor maps.

After sufficient agreement was obtained between calculated and observed F-values, we prepared an electron density projection $\rho(xz)$ using almost all $(h0l)$ reflections. Parameters thus found, when combined with $\rho(yz)$ already obtained, led us to a group of structures in which the benzene ring of the hydroquinone molecule was somewhat deformed. Thus we performed two series of extensive trial-and-error calculations in order to be sure whether this deformation was real or not. In one series of the calculation we always assumed a regular hexagon with sides 1.39Å for hydroquinone, while in the other no such assumption was made. The best model we obtained in each of the two series gave the values of reliability indices 0.158 and 0.154 respectively, both including the contribution of hydrogen atoms. The signs of F-values calculated from these two models differed only in two weak reflections out of 67 observed values, and the change in $\sum |F(h0l)|$ is only 0.6% if we neglect them. Hence we proceeded to the next stage omitting these two reflections.

The next step was to obtain the final x and z parameters for all the atoms. To do this we used the method of differential synthesis and applied the corrections for series-termination. This step was repeated twice. Carbon atom C_{IV}, which is linked to oxygen O_{II} to form a quinone molecule, was not resolved in $\rho(xz)$ projection (Fig. 3), so that x and z parameters for C_{IV} were obtained by least squares calculations treating only these two parameters as variables, after other atoms were all fixed.

The reliability index R obtained for $F(h0l)$ was reduced to 0.124 including the contributions of hydrogen atoms.

Determination of y Parameters—The determination of y parameters was much more troublesome. Although we had obtained by this stage (R=0.139 for $(0kl)$ including hydrogen atoms) fairly good parameters for all the atoms from trial-

5) G. Knott, *Proc. Phys. Soc.*, **52**, 229 (1940).
6) S. Banerjee, *Z. Krist.*, **100**, 316 (1939).

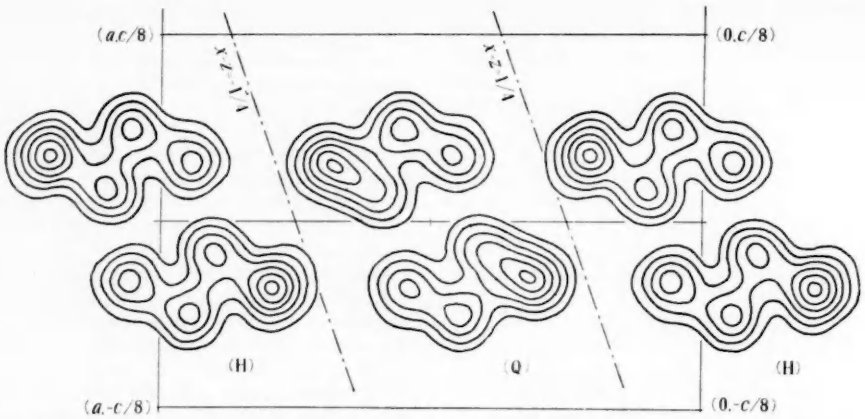

Fig. 3. Electron density projection $\rho(xz)$. Limiting planes for the bounded projections are also indicated by chain lines (see text).

and-error method, the refinement seemed to be hopeless when we used (0*kl*) reflections only, even by way of least squares calculations, since the component molecules overlap atom to atom almost completely in the projection along [100] (Fig. 4). However, we were able to overcome this difficulty using the method of bounded projection. This method was especially convenient in this structure, because, if we choose suitable limiting planes, we need only (*hkl*) intensities with h and l odd, which are all weak, and appropriate values for them can be estimated without too much difficulty. Actually, we prepared bounded projections in a modified form so as to separate quinone and hydroquinone completely. The projection was made along [100] axis, with the limiting planes at,

$$x-z=1/4 \text{ and } x-z=-1/4,$$

as indicated in Fig. 3. The expressions for these bounded projections are as follows:

$$B_I=\frac{2a}{V}\sum_{-k}^{k}\sum_{0}^{l}\sum_{-h}^{h}\int_{x=-\frac{1}{4}+z}^{x=\frac{1}{4}+z}F_{hkl}\cos 2\pi(hx+ky+lz)\,dx$$

$$=B_0+B_h$$

$$B_{II}=\frac{2a}{V}\sum_{-k}^{k}\sum_{0}^{l}\sum_{-h}^{h}\int_{x=-\frac{1}{4}+z}^{x=\frac{1}{4}+z}F_{hkl}\cos 2\pi(hx+ky+lz)\,dx$$

$$=B_0-B_h$$

where

$$B_0=\frac{a}{V}\sum_{-k}^{k}\sum_{0}^{l}F_{0kl}\cos 2\pi(ky+lz)$$

$$B_h=\frac{2a}{V}\sum_{-k}^{k}\sum_{1}^{l}\left[\sum_{\substack{-h\\(h\neq 0)}}^{h}\left(\begin{matrix}1\\ \pi h\end{matrix}\sin\frac{\pi h}{2}\right)F_{hkl}\right]$$

$$\times\cos 2\pi\{ky+(l+h)z\}$$

The intensities for (*hkl*) with $h=3$, 1, $\bar{1}$ and $\bar{3}$ collected from oscillation photographs were utilized after the application of necessary corrections. No effort was made to obtain data with h higher than these, as they did not seem to effect the results seriously. Signs of $F(hkl)$ were derived from calculated values using the best set of parameters obtained at that stage, contributions from hydrogen atoms being neglected. The first projection was calculated using x and z parameters which were obtained by differential Fourier syntheses, and the third and last one was calculated only along b axis through the atomic positions, after x and z parameters were all fixed. Termination corrections were also applied. y parameters thus obtained were listed in Table II together with the x and z parameters obtained in the previous section. Calculated and

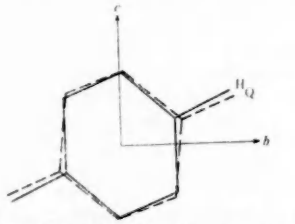

Fig. 4. Projection of the two component molecules along the a axis.
H: hydroquinone, Q: quinone.

TABLE II

FINAL ATOMIC CO-ORDINATES

	x	y	z		x	y	z
C_I	0.1039	0.1640	0.0216	C_V	0.5523	0.0121	0.0621
C_{II}	0.0518	0.0077	0.0610	C_{VI}	0.5439	0.1632	−0.0453
C_{III}	0.0549	0.1695	−0.0412	O_I	0.2128	0.3355	0.0440
C_{IV}	0.6021	0.1854	0.0195	O_{II}	0.6849	0.3496	0.0374

TABLE III

OBSERVED AND CALCULATED F-VALUES FOR ZONAL REFLECTIONS

$0k$ l	$\lvert F_{obs}\rvert$	F_{calc}	$0k$ l	$\lvert F_{obs}\rvert$	F_{calc}	$h0$ l	$\lvert F_{obs}\rvert$	F_{calc}	$h0$ l	$\lvert F_{obs}\rvert$	F_{calc}
00. 4	122	142	01. 2	54	−63	10. 1	12	−13	$\bar{1}$0. 3	5	− 1
8	82	−85	4	37	−45	5	8	− 5	7	3	− 1
12	72	83	6	29	−17	9	9	9	11	11	−11
16	15	−12	8	47	−60	13	12	12	15	10	−10
20	6	6	10	13	− 5	17	2	3	19	0	− 1
24	3	0	12	31	−31	21	5	− 5	23	6	6
			14	20	19	25	7	− 5			
02. 0	32	−37	16	10	−12						
2	39	41	18	15	8	20. 2	24	−22	$\bar{2}$0. 2	92	79
4	47	−52	20	7	− 4	6	92	−85	6	35	39
6	59	73	22	14	−17	10	42	−34	10	26	32
8	23	−17	24	0	3	14	9	11	14	33	31
10	16	17	26	14	−15	18	4	− 4	18	32	26
12	26	25				22	19	−14	22	0	3
14	39	−41	03. 2	13	17						
16	34	33	4	13	−14	30. 3	21	21	$\bar{3}$0. 1	0	2
18	38	−45	6	36	−40	7	22	21	5	8	− 7
20	3	1	8	0	− 3	11	0	0	9	4	− 3
22	15	−15	10	35	−33	15	12	−13	13	5	− 1
24	15	−13	12	4	− 5	19	6	−10	17	5	− 4
26	12	10	14	15	8				21	0	− 2
			16	0	5	40. 0	0	2			
04. 0	16	−22	18	24	16	4	21	22	$\bar{4}$0. 4	42	−39
2	22	23	20	0	2	8	13	11	8	63	−71
4	30	−28	22	0	3	12	5	− 6	12	25	−24
6	32	34	24	3	1	16	23	−26	16	40	42
8	10	− 8				20	20	−19	20	50	48
10	3	3	05. 2	29	27						
12	28	24	4	7	8	50. 1	8	− 8	$\bar{5}$0. 3	7	8
14	33	33	6	0	− 3	5	17	−19	7	11	11
16	24	26	8	17	17	9	6	− 8	11	10	13
18	25	27	10	5	−10	13	9	8	15	0	− 1
20	4	−19	12	15	17	17	10	13	19	0	0
22	9	7	14	3	4						
24	12	12	16	5	6	60. 2	37	28	$\bar{6}$0. 2	8	− 4
			18	0	3	6	8	−11	6	0	5
06. 0	42	56	20	0	− 2	10	19	18	10	21	−16
2	9	− 7				14	12	13	14	18	−19
4	22	25	07. 2	4	5	18	0	− 1	18	2	0
6	11	−11	4	7	− 7						
8	22	−20	6	8	− 5	70. 3	0	− 2	$\bar{7}$0. 1	10	−11
10	4	− 3	8	7	− 6	7	9	10	5	8	− 8
12	22	−22	10	5	− 4	11	10	13	9	0	1
14	0	1	12	4	− 4	15	4	4	13	0	4
16	4	− 3									
						80. 0	21	−24	$\bar{8}$0. 4	16	−16
						4	6	5	8	0	2
						8	33	36			

TABLE IV
OBSERVED AND CALCULATED F-VALUES FOR hkl REFLECTIONS

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
11.	1	6	− 4
	3	9	8
	5	7	11
	7	3	0
	9	18	20
	11	10	−10
	13	11	8
	15	12	−10
	17	5	− 4
	19	0	− 3
	21	9	− 8
	23	2	3
	25	5	− 4
	27	3	4
12.	1	6	6
	3	10	−12
	5	6	15
	7	17	−18
	9	4	0
	11	5	− 5
	13	9	− 5
	15	11	9
	17	0	− 3
	19	11	11
	21	2	0
	23	2	3
13.	1	3	5
	3	10	− 8
	5	0	− 1
	7	5	− 4
	9	7	− 7
	11	8	9
	13	6	− 7
	15	15	13
	17	2	− 3
	19	10	7
	21	0	0
	23	2	− 4
14.	1	0	1
	3	2	− 1
	5	2	− 2
	7	6	3
	9	7	− 7
	11	0	0
	13	6	− 4
	15	7	− 4
	17	3	4
	19	7	− 5
	21	8	7

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
$\bar{1}$1.	1	5	8
	3	4	3
	5	7	9
	7	2	− 3
	9	7	7
	11	2	0
	13	0	1
	15	8	6
	17	5	− 4
	19	4	4
	21	3	− 4
	23	0	0
	25	2	2
	27	3	− 2
$\bar{1}$2.	1	0	2
	3	0	− 1
	5	0	0
	7	0	1
	9	0	0
	11	6	6
	13	3	− 5
	15	7	6
	17	9	− 8
	19	4	3
	21	6	− 5
	23	0	− 2
$\bar{1}$3.	1	3	− 3
	3	0	− 2
	5	0	0
	7	0	0
	9	7	− 4
	11	2	2
	13	6	− 3
	15	0	0
	17	6	4
	19	0	− 2
	21	9	7
	23	2	− 3
$\bar{1}$4.	1	4	6
	3	0	0
	5	0	0
	7	0	− 2
	9	8	− 6
	11	0	− 2
	13	2	− 3
	15	0	− 1
	17	3	3
	19	0	0
	21	5	4

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
15.	1	5	4
	3	0	3
	5	0	2
	7	4	5
	9	4	− 3
	11	0	1
	13	0	− 1
	15	0	− 2
	17	4	4
16.	1	0	0
	3	10	11
	5	0	− 2
	7	6	8
	9	0	0
	11	0	2
	13	2	2
	15	0	− 1
17.	1	2	− 2
	3	6	2
	5	0	1
	7	0	1
	9	0	4
31.	1	10	−13
	3	1	1
	5	13	−13
	7	14	−14
	9	3	− 1
	11	11	−12
	13	8	9
	15	3	2
	17	9	8
	19	9	9
	21	3	0
	23	5	4
32.	1	13	−11
	3	9	− 9
	5	0	3
	7	12	−14
	9	16	17
	11	5	− 6
	13	17	16
	15	6	4
	17	4	3
	19	6	6
	21	8	− 7
	23	0	0

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
$\bar{1}$5.	1	5	− 5
	3	2	1
	5	8	− 9
	7	2	3
	9	4	− 7
	11	0	0
	13	0	− 2
	15	2	− 2
	17	2	2
$\bar{1}$6.	1	5	− 5
	3	2	3
	5	0	3
	7	2	3
	9	4	5
	11	2	− 2
	13	5	5
	15	5	− 4
$\bar{1}$7.	1	5	5
	3	6	2
	5	8	7
	7	0	0
	9	6	6
$\bar{3}$1.	1	10	−15
	3	0	− 2
	5	7	− 6
	7	6	5
	9	1	1
	11	0	3
	13	0	− 2
	15	5	1
	17	2	− 5
	19	2	2
	21	0	− 3
	23	5	2
$\bar{3}$2.	1	0	3
	3	13	13
	5	6	7
	7	7	6
	9	3	4
	11	2	1
	13	0	0
	15	0	− 1
	17	0	1
	19	2	− 3
	21	4	3
	23	6	− 4

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
33.	1	12	12
	3	3	− 8
	5	14	14
	7	4	− 8
	9	0	− 1
	11	0	− 2
	13	13	−12
	15	0	4
	17	7	− 8
	19	2	5
	21	0	0
34.	1	8	9
	3	2	− 2
	5	4	2
	7	0	1
	9	10	−10
	11	2	6
	13	9	−11
	15	8	8

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
$3\bar{3}$.	1	1	3
	3	0	− 1
	5	0	0
	7	3	− 5
	9	0	− 1
	11	0	− 1
	13	0	0
	15	0	1
	17	0	1
	19	0	− 1
	21	0	1
$3\bar{4}$.	1	0	− 3
	3	2	− 3
	5	2	− 3
	7	3	5
	9	0	− 3
	11	0	4
	13	0	− 2
	15	0	0

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
34	17	0	− 2
	19	8	5
35.	1	0	4
	3	4	5
	5	0	1
	7	8	8
	9	0	0
	11	7	4
	13	4	2
	15	4	− 3
	17	0	3
36.	1	0	2
	3	4	3
	5	0	− 1
	7	3	4
	9	0	− 2
	11	0	1

hk	l	$\lvert F_{obs}\rvert$	F_{calc}
$3\bar{4}$	17	0	0
	19	0	0
$3\bar{5}$.	1	0	0
	3	0	4
	5	0	2
	7	0	− 1
	9	0	− 1
	11	5	− 6
	13	0	− 1
	15	7	− 6
	17	1	2
$3\bar{6}$.	1	0	− 1
	3	2	− 5
	5	2	− 2
	7	6	− 6
	9	0	0
	11	6	− 6

observed F-values are given in Tables III and IV.

Tests on the Semiquinone-type structure.—Another type of structure consisting of semiquinone-type molecules was also checked by trial calculations followed by differential Fourier syntheses. After two steps of approximations we were able to obtain a parameter set with reliability index $R=0.24$ for ($h0l$) reflections neglecting the contributions of hydrogen atoms, while that for the correct structure was 0.15. If we devide F-values into groups of even and odd reflections we find for the semiquinone type (excluding hydrogen atoms) $R(\text{even})=0.19$ and $R(\text{odd})=0.55$, as compared with those of the other (excluding hydrogen atoms) $R(\text{even})=0.15$ and $R(\text{odd})=0.16$. The R-value for the reflections with h odd is exceedingly large in the case of semiquinone-type. It may be considered as an indication that the structure of this type is wrong as to the structural features especially responsible for these reflections, that is, as to the deviations from the averaged structure.

Collection of intensity data.—Most of the intensity data were collected from two sets of oscillation photographs about a and b axes. In order to obtain good intensity estimates even for weaker reflections with h and l odd, we prepared, for each range of oscillation, a photograph of very long exposure in addition to a usual one. A rotation photograph was taken about the a axis using multiple-film technique. This provided further confirmation and gave measurable intensities even for very strong reflections. All these data were combined and served for most part of the present work.

During the course of analysis, however, it was found that the specimen showed a strong extinction. Additional sets of oscillation photographs were then prepared for both a and b axes using a tiny crystal dipped into liquid air several times. The disagreement between calculated and observed F-values for strongest reflections became less remarkable, but we were unable to eliminate the effect of extinction completely.

All the photographs were prepared using Cu-K radiations, with or without a nickel filter, and the intensities were estimated by comparing them visually with a series of standard intensity scales, except in measuring rotation photographs where a recording microphotometer was used. The number of reflections actually observed as compared with what were possible is listed below:

type of reflections	number of reflections observed	possible
$0kl$	74	83
$h0l$ (h and l even)	39	44
$h0l$ (odd)	33	42
$1kl$, $\bar{1}kl$ ($k=0$)	100	142
$3kl$, $\bar{3}kl$	73	120

Description and Discussion of the Structure

The structure of quinhydrone obtained here consists of two sorts of molecules, quinone and hydroquinone, of which the latter appears to be deformed to some extent as is shown in Fig. 5. The average plane of six carbon atoms of quinone with its center at 1/4, 0, 0 is given by the equation

$$-0.836(ax-3.837)+0.507by+0.210cz'=0,$$

where the z' axis was taken perpendicular to x and the oxygen O_{II} comes by 0.055Å

outside of the plane. The difference between the two C-C(H) bond lengths adjacent to the C=O group is scarcely significant and the mean value 1.465Å is rather short in comparison with 1.50 Å reported for *p*-benzoquinone[7]. This is probably related to the observed elongation of $C_V=C_{VI}'$ bond from the standard value 1.32 Å to 1.335 Å, though the difference is hardly significant. C=O bond length 1.234Å observed is a value commonly found for the carboxyl group forming a hydrogen bond, though somewhat shorter value 1.15Å is reported for *p*-benzoquinone. The average plane containing six carbon atoms of the hydroquinone molecule with its center at the origin is given by

$$-0.811ax+0.542by+0.219\,cz'=0$$

The oxygen atom O_I calculated to be only 0.014Å outside the plane may well be considered to be almost coplanar with the benzene ring. The observed C-O(H) distance 1.409Å is considerably larger than the usual 1.36Å for a phenolic C-O, which may possibly be related to the deformation of the benzenoid ring described below.

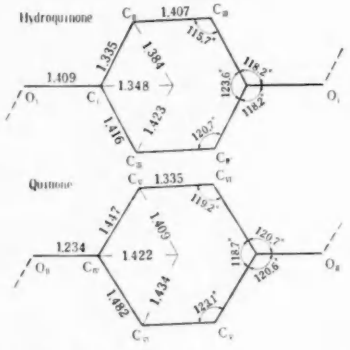

Fig. 5. Shape of the component molecules. Hydrogen bonds are indicated by broken lines.

A rather striking feature is the deformation of the benzenoid ring of the hydroquinone molecule. In fact, the bond length C_I-C_{II} is contracted to 1.335Å, while C_I-C_{III} and $C_{II}-C_{III}'$ are 1.416 and 1.407Å respectively, and they seem to be elongated somewhat. Further, the angle $C_I-C_{III}-C_{II}'$ is found to be 115.7° and as a result of these changes, the benzenoid ring rather resembles a quinoid ring. Although the cause of this deformation is not yet clear, it will be interesting to add here that the C_I-C_{II} bond, which appears shorter than C_I-C_{III}, is nearly parallel to the hydrogen bond O-H···O which will be described in the next paragraph. A similar deformation was also reported in the case of 1, 4-dimethoxybenzene (Fig. 6) by Robertson and others[8] although they did not try to explain it. We may mention in this connection that Tomiie[9] pointed out once that the lone-pair electrons at the oxygen atom may possibly influence the benzenoid ring to stabilize one of the resonance forms.

Fig. 6. Shape of 1,4-dimethoxybenzene after Robertson.

The two sorts of molecules, quinone and hydroquinone, are linked alternately through O-H···O hydrogen bonds of moderate length (2.71Å) to form a zigzag chain which is extended throughout the crystal*. Fig. 7 (a) is a part of the structure at $z=0$ and shows that these chains are running along [120]. Planes of molecules of the same sort are all parallel within a single chain, since they correspond to some translation of the crystal lattice, while those of one sort are tilted slightly (about 2°30′) with respect to those of the other. Fig. 7 (b) shows a part of the similar sheet at $z=1/4$, but in this case, the chains are seen to be running along $[\bar{1}20]$

Fig. 7 (a) also shows how these chains are stacked side by side to form a molecular sheet parallel to (001). These sheets are again piled up into a sort of layer lattice. A perspective view of a part of the structure is given in Fig. 8.

Between the neighboring sheets, the nearest approach distances are those between non-bonded carbon and oxygen atoms of lengths 3.31~3.83Å as shown in Fig. 8. These values are comparable with 3.4Å reported by Robertson in *p*-benzoquinone[7]

7) J. M. Robertson, *Proc. Roy. Soc.*, **A150**, 106 (1953).

8) T. H. Goodwin, M. Przybylska and J. M. Robertson, *Acta Cryst.*, **3**, 279 (1950).

9) Y. Tomiie, informal discussion.

* Such a chain-like structure is often accompanied by marked thermal motion of the molecular plane, which was actually observed in the present case as strong diffuse scattering on both Laue and oscillation photographs.

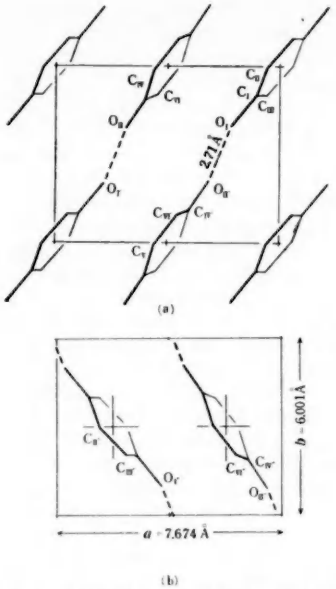

Fig. 7. Part of the molecular sheet at $z=0$ (a) and $z=1/4$ (b).

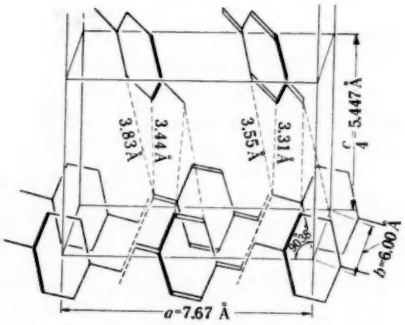

Fig. 8. Perspective view of a part of the structure of quinhydrone.

and with 3.24 and 3.39Å given by Abrahams in *p*-dinitrobenzene.[10] Similar values are often found between aromatic carbon and oxygen atoms and do not seem to be exceptionally short. Only it will be interesting to notice here that the oxygen atom of one sort of molecule always has the carbon atoms of the other as its neighbors. No C···C or O···O distances are shorter than 4Å between the neighboring sheets.

Hitherto we have seen that the crystal of quinhydrone is a sort of layer structure containing hydrogen bonds. Suzuki and Seki[11] determined the heat of formation of crystalline quinhydrone and estimated that the hydrogen-bond energy seems to contribute to a considerable part to it. But the remarkably compact structure, suggested by the observed density 1.401 in comparison with those of hydroquinone 1.33 and quinone 1.32, and the characteristic coloring of quinhydrone are not explained by hydrogen bonds.

Another type of interaction also seems to be taking place within the molecular sheet. We have already mentioned that the two component molecules are piled up alternately along the *a* axis, and overlap atom to atom almost completely when projected along this axis (Fig. 4). The planes of adjacent molecules are nearly parallel (inclination about 2°30′) and the perpendicular distance between the averaged molecular plane is measured to be 3.16Å. This value is remarkably short for an interplanar distance of aromatic molecules which is usually found to be larger than 3.4Å and may not have been realized without a considerable attraction between these molecules, if the repulsive forces are assumed to be the same. We may thus consider that these component molecules are linked in some way along the *a* axis and make up a sort of molecular column of alternating quinone and hydroquinone molecules along this direction. Or we may even look upon the structure of quinhydrone as consisting of such columns linked side by side through hydrogen bonds to form a sheet. Similar columns are also found in the molecular compound analyzed by Powell et al.[2] which does not contain hydrogen bonds. So that the existence of such columns may be looked upon to be a characteristic feature of these types of molecular compounds.

Now let us look into the detailed structure of the molecular column in quinhydrone. Fig. 9 is the projection of two

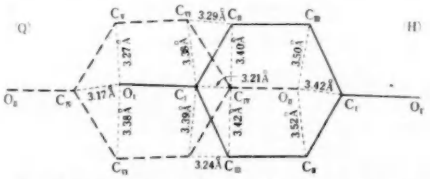

Fig 9. Perpendicular projection of two neighboring molecules within a column.

10) S. C. Abrahams, *Acta Cryst.*, **3**, 194 (1950); F. J. Llwellyn, *J. Chem. Soc.*, **1947**, 884.

11) K. Suzuki and S. Seki, This Bulletin, **26**, 372 (1953).

succeeding molecules within a column upon the mean molecular plane and shows the relative positions of the stacking molecule more clearly. Here, it must be born in mind that each molecule lies on the center of symmetry, so that each component molecule is sandwiched between molecules of the other component on both sides. Atomic distances between the molecules are also given in the figure. C···O distances found here are not very different from those between the molecular sheets. But the intermolecular C···C distances so short as those given here do not seem to have been reported before except in 3:4-benzophenanthrene.[12]

Nakamoto[13] investigated the optical dichroism of quinhydrone and some other molecular compounds of similar type and concluded that, in these substances, π-electrons are more mobile in the direction perpendicular to the plane than in the plane of the molecule, contrary to the case of ordinary aromatic compounds, where π-electrons are more mobile along the molecular plane. This result, as was pointed out by himself, will be explained qualitatively if we assume that the characteristic absorption in quinhydrone is due to a stable complex which is made up from quinone and hydroquinone through the mechanism of charge-transfer proposed by Mulliken.[14] Also the observed short intermolecular distance will be explained by this concept.

But why, then, is an unusually stable complex formed in the case of quinhydrone? A theoretical treatment by Suzuki[15] seems to answer the essential points of this question. He extended the treatment of Mulliken to the case of an infinite chain and calculated the electronic state of quinhydrone to the Bloch approximation and concluded that in the excited state most of the mobile electrons are transferred from hydroquinone to quinone molecule, so that the observed spectra (maximum approximately at 550 and 380 mμ) correspond to the intermolecular charge-transfer spectra. In other words, he concludes that the attraction between the two components in quinhydrone may be due to the interaction between the highest occupied molecular orbital level of hydroquinone and the lowest unoccupied one of the quinone molecule, and that the very strong interaction in this case may probably be attributed to the fact that the molecular orbitals of quinone and hydroquinone have the same symmetry and, at the same time, their energy difference is small.

Thus, we have in quinhydrone a remarkable example of a series of molecular compounds of which combined investigations of the crystal structure and of physical properties seem to be worth performing.

The authors would like to express their sincere thanks to Professor Akabori of Osaka University for his interest and constant encouragement especially of one of them (H. M.). Their thanks are also due to the Ministry of Education, to which they owe a part of the cost of this work.

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12) F. H. Herbstein and G. M. Schmidt, *J. Chem. Soc.*, **1954**, 3302.
13) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952).
14) R. S. Mulliken, ibid., **74**, 811 (1952).
15) K. Suzuki, *Busseironkenkyu*, No. **102**, p. 5 (1956), (in Japanese).

Refining of Low Temperature Cresol No. 1

By Keisho YAMADA

(Received November 18, 1957)

The low temperature cresol No. 1 has an offensive smell and a strong tendency of spontaneous coloration. According to Funakubo et al.[1], coloration of tar-acid oil occurs in the presence of acetic and formic acids, and more rapidly when the oil is exposed to the sunlight or contains a trace of iron together with acetic and formic acids. It has been stated by Lunge[2] that coloration of phenol has its origin in ferric benzoate formed from benzoic acid in the tar-acid oil and iron from distilling equipments, and he referred to indene as another source. According to Ueda et al.[3], coloration of tar-acid oil is caused chiefly by pyrrol, and in the case of low-temperature tar, catechol also partakes of its cause. Jaeger[4] said that coloration of tar occurs chiefly by oxygen in the air and basic oil promotes the coloration.

Egloff et al.[5] reports that spontaneous coloration of gasoline is due to free sulfur and alkyl disulfides, and when both are present, remarkable coloration takes place. According to Suzuki et al.[6], an offensive smell of low temperature tar is due to thiophenols.

The investigations of impurities in the coal tar products have become the topics of interest in recent years. However, only a little literature has been published on the inquiries of impurities in the low temperature cresol No. 1 which may cause the offensive smell and coloration.

The present paper is the report on the researches of the impurities which may deteriorate the quality of low temperature cresol No. 1, and on the suitable method for removing them.

This study revealed about thirty substances as impurities in the low temperature cresol No. 1, including those which have not been certified in coal tar up to the present. Several of them showed remarkable spontaneous coloration and strong peculiar smells, and these substances together with other unstable materials, which may cause the disgusting smell and coloration, were successfully removed by oxidation and active-clay treatment. The impurities in this refined cresol were investigated, and it was found that most of them were removed.

The author has reported the results of his inspections of the impurities in the low temperature cresol No. 1 in the Journal of the Chem. Soc. of Japan, Ind. Chem. Sec. from part 1 to 7, and in this paper the results have been summarized and discussed further.

Experimental Results

(1) Preparation and Properties of Low Temperature Cresol No. 1—At the Nitrogen Factory of Ube Industries, Ltd., the low temperature cresol No. 1 is prepared by the way shown in Tables I and II. The low temperature cresol No. 1 has an offensive smell and a dark brown color, and its specific gravity is 1.036 at 24°C. Engler's distillation curve is shown in Fig. 1.

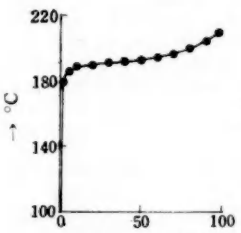


Fig. 1. Engler's distillation curve.

Immediately after distillation, the low temperature cresol No. 1 is a colorless and transparent oil, but gradually it begins to color on storage in the open air, and finally becomes an opaque black brown oil. In a dark place, however, its color turns only a light yellowish red in thirty days after distillation, which is lighter than the coloration caused by leaving the distillate

1) E. Funakubo and G. Kawasaki, unpublished data.
2) G. Lunge, "Coal-Tar and Ammonia" Part I, Gurney and Jackson, London, (1916), p. 266.
3) T. Ueda and H. Matsuda, Japanese Patent No. 199, 897.
4) A. Jaeger, *Brenn. Chem.*, **1**, 257 (1923).
5) G. Egloff, J. C. Morrell, W. L. Benedict and C. Wirth, U. O. P. Booklet No. 35, Universal Oil products Company, Chicago, (1938).
6) M. Suzuki, F. Kitahara and M. Koga, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zassi*), **55**, 28 (1952).

TABLE I
SEPARATION OF CRUDE ACID OIL FROM LOW-TEMPERATURE TAR

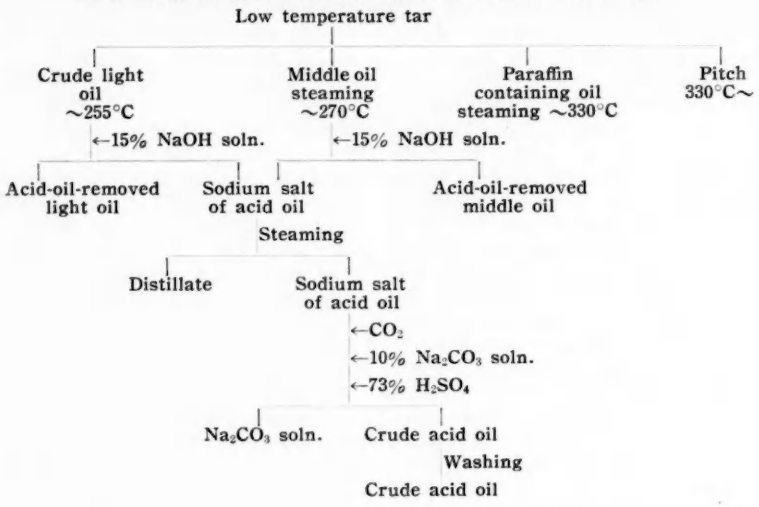
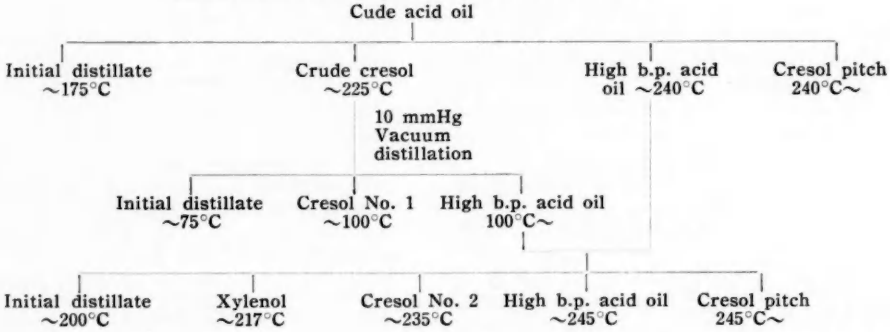


TABLE II
PREPARATION OF LOW TEMPERATURE CRESOL No. 1



in the air for one day. When the low temperature cresol No. 1. is distilled under a stream of nitrogen or carbon dioxide, and the distillate is stored in a glass bottle, containing nitrogen or carbon dioxide, the coloration does not develop in thirty days after distillation, and the distillate remains colorless and transparent just as it is immediate after distillation. On the other hand, the low temperature cresol No. 1 absorbs a considerable amount of oxygen, and the coloration is nearly proportional to the amount of absorbed oxygen[7].

In the case of lack of either light or oxygen, the low temperature cresol No. 1 is stable enough against coloration. So, it is clear that the remarkable coloration occurs only when both light and oxygen are present.

According to Amemiya et al.[8], for example, the components of low temperature cresol No. 1 are: 23 weight% of phenol, 8 of *o*-cresol, 22 of *m*-cresol, 11 of *p*-cresol and 31 of xylenols and the higher homologs, (including 5% operation loss). The impurities in the low temperature cresol No. 1 were determined by the method listed in Tables III and IV. The composition was 0.217 volume % of strong acid oil, 0.367 of weak acid oil, 0.733 of neutral oil and 0.033 of basic oil, and the total impurities were 1.350 volume %. The 176~210°C fraction of normal acid oil obtained by removing these impurities from the low temperature cresol No. 1, did not color even when it was left in the open air[9], and had no more offensive smell. Thus it is indicated that the materials included in these impurities cause an offensive smell and spontaneous coloration.

(2) Identification of the Constituents of

7) K. Yamada, ibid., **60**, 1319 (1957).
8) J. Amemiya, E. Tunetomi and T. Nagazawa, *J. Japan Tar Ind. Association*, **4**, 104 (1952).
9) K. Yamada, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zassi*), **60**, 591 (1957).
10) K. Yamada, ibid., **60**, 921 (1957).

TABLE III

SEPARATION OF STRONG ACID OIL, NORMAL ACID OIL

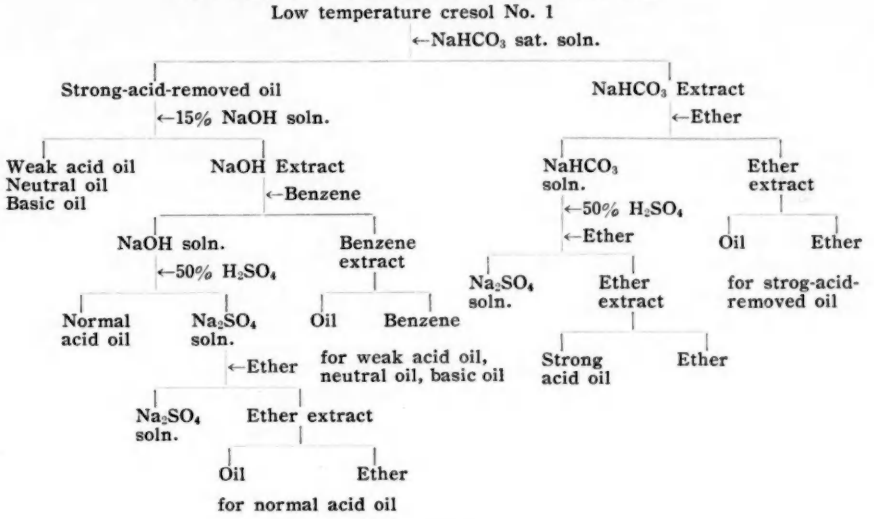


TABLE IV

SEPARATION OF WEAK ACID OIL, NEUTRAL OIL, BASIC OIL FROM BENZENE EXTRACT

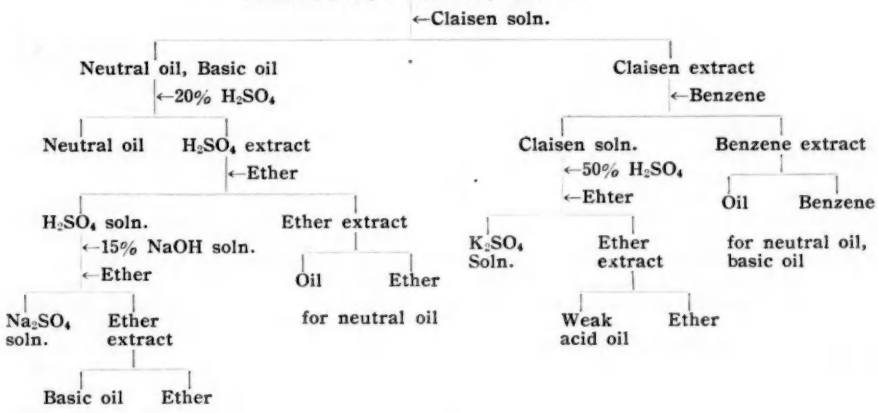


TABLE V

SULFUR CONTENT IN SEVERAL SAMPLES (wt. %)

Sample	(1) Low temperature cresol No. 1	(2) Lower boiling fraction	(3) Medium fraction	(4) Residue
Total S (A)	0.0427	0.0183	0.0160	0.0792
Hydrogen sulfide S	0.0003	0.0004	0.0001	0.0000
Elementary S	0.0070	0.0059	0.0054	0.0059
Mercaptan S	0.0061	0.0045	0.0036	0.0032
Disulfide S	0.0012	0.0010	0.0008	0.0010
Sulfide S	0.0004	0.0005	0.0004	0.0005
Thiophene S	0.0010	0.0005	0.0004	0.0010
Sum up (B)	0.0160	0.0128	0.0107	0.0116
Total S in Residue (A−B)	0.0267	0.0055	0.0053	0.0676
B/A	37.4	69.9	66.8	14.7

the Impurities.—*a*) *Strong Acid Oil.*—The distillation curve of the strong acid oil is similar to that of the low temperature cresol No. 1, but the former is contained chiefly in the lower boiling fraction of the low temperature cresol No. 1.[10] Strong acid oil has an offensive and stimulative smell like rancid butter.

Several acidic impurities such as propionic, *iso*-butyric, *n*-butyric, *iso*-valeric, *n*-valeric acids and catechol were detected in the strong acid oil by means of rectification, specific gravity, refractive index, neutralization value, bromine number, paper chromatography, melting point of the corresponding derivatives (amides), mixed-melting point test with the corresponding authentic samples, ultraviolet absorption spectra and infrared absorption spectra of each fraction[10].

The iodine number of the carboxylic acid fraction isolated by esterification, hydrolysis and extraction, was 110.2. On heating, the strong acid oil forms polymeric material; this fact suggests the presence of unsaturated acids.

b) *Weak Acid Oil.*—Weak acid oil in impurities was rectified, and the specific gravity, the refractive index, the boiling point, the average molecular weight and the hydroxyl value of each fraction were determined; furthermore qualitative test (ferric chloride test), melting-point test of the derivatives (phenoxy acetic acids) and mixed-melting point test with the corresponding authentic samples were also made. Upon these experiments, the presence of *p*-cresol, 2,4- and 2,5-dimethylphenols was noticed[11].

It seems that *p*-cresol, because of its small dissociation constant, intrudes into weak acid oil in the course of separation based on the said method. The rest of the components of the weak acid oil are supposed to be higher boiling phenols such as dimethylphenols, trimethylphenols, ethylphenols and methylethylphenols.

c) *Neutral Oil.*—The distillation curve of the neutral oil shows that fractions below 176°C, as well as fractions above 210°C and residue, occupy a considerable amount of the total distillate, and that medium fractions (176~210°C) take a much smaller part, though this temperature range corresponds to the main fraction of the low temperature cresol No. 1[11].

So it is possible to say that a considerable amount of unstable materials which polymerize easily by heating, is included in the neutral oil. The neutral oil was rectified and the specific gravity, the refractive index, the sulfur content, the absorption loss by sulfuric acid and the iodine number of each fraction were determined. There was a great deal of absorption loss by both 80 and 98% sulfuric acid; especially the lower boiling fractions were absorbed more by 80% sulfuric acid, and showed high iodine numbers[11,12].

Every fraction was distinctly positive to silver mirror test and Schiff's reagent test. Carbonyl compounds in the neutral oil were investigated, through melting-point check of the derivatives (2,4-dinitrophenylhydrazones or semicarbazones) and mixed-melting point test with the corresponding authentic samples. Thus *n*-propyl methyl ketone, mesityl oxide, *n*-amyl methyl ketone, *iso*-butyl methyl ketone, *o*-hydroxybenzaldehyde, benzaldehyde, 4-methylcyclohexanone and acetophenone were detected in the neutral oil[11,12].

By the same research tests, aromatic hydrocarbons in the neutral oil were identified as *p*-xylene (*O*-aroyl tetrachlorobenzoic acid), mesitylene (*O*-aroyl benzoic acid) and naphthalene[11] (picrate).

d) *Basic Oil.*—Forty nine volume per cent of the basic oil runs out below 150°C and 71% below 176°C in contrast to the case of the low temperature cresol No. 1 which gives a little distillate below 176°C[13].

Through several tests as described in the previous sections and of derivatives (mercuric chloride complexes and picrates), 2-, 3-, 4-methylpyridines, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-dimethylpyridines, 4-ethylpyridine and 2,4,6-trimethylpyridine were identified in the basic oil[13].

e) *Sulfur Compounds.*—The low temperature cresol No. 1 contains 0.0427 weight % of sulfur. Concerning spontaneous coloration, each fraction of the low temperature cresol No. 1 and classified impurities were studied. On the other hand, sulfur content was measured in each sample. As a result it was found that the degree of coloration is nearly parallel to sulfur content[14]. Sulfur contents measured in conformity with their chemical forms are shown in Table V. Four samples were checked: (1) low temperature cresol No. 1, (2) its lower boiling fraction (15 volume %), (3) medium fraction (50%), (4) residue (33%) (water 1 %, loss 1%).

According to Table V, it is understood that all of them contain free sulfur and mercaptans as predominant constituents, alkyldisulfides as next, and a little of hydrogen sulfide, alkyl sulfides and thiophenes are also contained.

(3) Purification by Oxydation.—*a*) *Spontaneous Coloration of the Refined Cresol.*—As stated above, the coloration of the low temperature cresol No. 1 hardly ever occurs in the absence of oxygen, even if it is exposed to the sunlight. It absorbs a considerable amount of oxygen and the relation between coloration and absorbed oxygen is almost proportional. These facts led to the idea that the impurities which bring about spontaneous coloration by absorbing oxygen, are to be removed by the use of enough amount of oxidizing agent, followed by adsorption of the products on active clay.

As the oxidizing agent, potassium cyanoferrate or sodium bichromate was used. Adopting one of the oxidizing agents only, or active clay only, or both substances, purification by oxidation was carried out in several cases. The most preferable result was obtained when the low temperature cresol No. 1 was treated with 0.2% of potassium cyanoferrate together with 5% of

11) K. Yamada, ibid., **60**, 1314 (1957).

12) K. Yamada, ibid., **61**, 269 (1958).
13) K. Yamada, ibid., **60**, 1310 (1957).
14) K. Yamada, ibid., **60**, 925 (1957).

active clay, and, after filtration, the distillate of 176~210°C (90 volume % of yield) was collected[7]. The product was named "Refined Cresol".

Hourly change of color was examined on four samples. They are: (1) above-mentioned refined cresol, (2) 176~210°C distillate of the low temperature cresol No. 1, (3) medium 50% of the distillate (25~75 volume %) of the first class *m*-cresol (97 % of this was distilled at 201~202°C), (4) 176~210°C distillate of the normal acid oil which was prepared by removing strong acid oil, weak acid oil, neutral oil and basic oil from the low temperature cresol No. 1.

Using spectrophotometer, transmissions at wave lengths 420, 470, 520, 580, 620 and 700 mμ were measured, and by their mean value, the degree of coloration was represented. Fig. 2 shows the results obtained when the samples were placed by the window to be exposed to the sunlight and Fig. 3 shows that obtained when they were exposed to the ultraviolet rays.

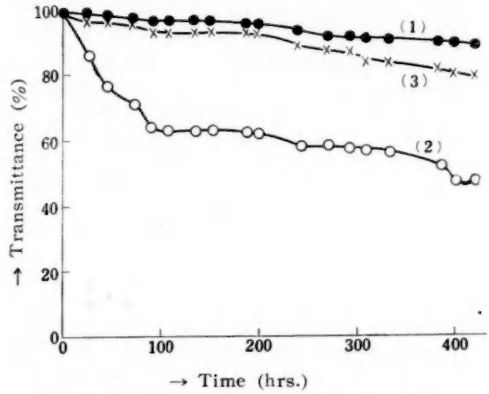


Fig. 2. Spontaneous coloration by the sunlight.
(1) ● Refined cresol
(2) ○ Low temperature cresol No. 1
(3) × *m*-cresol

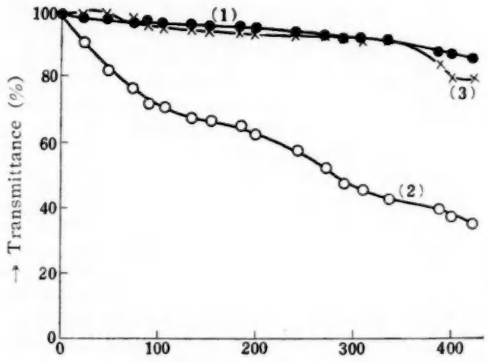


Fig. 3. Spontaneous coloration by the ultraviolet rays.
(1) ● Refined cresol
(2) ○ Low temperature cresol No. 1
(3) × *m*-cresol

As the refined cresol and the normal acid oil free from the impurities gave nearly equal results, the description of the latter was omitted.

Figs. 2 and 3 indicate that the coloration of the refined cresol advances very little. Therefore, most of the impurities which influence the spontaneous coloration of the low temperature cresol No. 1 seem to be eliminated by this operation.

TABLE VI
IMPURITIES IN THE REFINED CRESOL (vol. %)

	Low temperature cresol No. 1	Refined cresol
Strong acid oil	0.217	0.154
Normal acid oil	95.133	95.749
Weak acid oil	0.367	0.403
Neutral oil	0.733	0.411
Basic oil	0.033	0
Total impurities	1.350	0.968
Sum up	96.483	96.717
(Loss)	(3.517)	(3.283)

TABLE VII
SULFUR CONTENT IN THE REFINED CRESOL
(wt. %)

Sample	Low temperature cresol No. 1	Refined cresol
Total S (A)	0.0427	0.0151
Hydrogen sulfide S	0.0003	0.0001
Elementary S	0.0070	0.0042
Mercaptan S	0.0061	0.0026
Disulfide S	0.0012	0.0007
Sulfide S	0.0004	0.0002
Thiophene S	0.0010	0.0005
Sum up (B)	0.0160	0.0083
Total S in Residue (A−B)	0.0267	0.0068
B/A	37.4	55.0

b) Impurities in the Refined Cresol.—Impurities and sulfur compounds in the refined cresol are shown in Tables VI and VII.

Results and Discussion

(1) Formation of the Impurities.—As shown in Tables I and II, sodium salts of the strong acid oil are formed by adding 15% sodium hydroxide solution to the crude light oil and the middle oil. When carbon dioxide is introduced to the sodium salts, normal acid oil is separated as an oil layer, but owing to weak acidity of carbon dioxide the sodium salts of the strong acid oil remain in the same form in aqueous layer and are rejected together with the waste liquor of the sodium carbonate.

A small amount of sodium salts of the

strong acid oil still remaining is removed by washing with 10% sodium carbonate aqueous solution, but a portion of the sodium salts remains in the crude acid oil. These sodium salts change to the strong acid oil at the time of 73% sulfuric acid washing, and they form strong acidic impurities in the normal acid oil.

Weak acid oil is accompanied by the normal acid oil as it has the same chemical properties except for possessing slightly higher boiling point than that of the normal acid oil.

Neutral oil which comes through dissolution or mixing into the sodium salts of the acid oil, is removed at the steaming of the sodium salt, but their portion remains through dissolution and become neutral impurities in the normal acid oil.

A typical composition of the crude light oil shown in Table I is 47.5 volume % of acid oil, 2.0 of basic oil and 50.5 of neutral oil; of this neutral oil, 12.2 and 46.3 volume% are the parts absorbed by 80 and 98% sulfuric acid respectively, so that 41.5 volume% of the neutral oil is the unabsorbed part by 98% sulfuric acid. On the other hand the typical composition of the oil (distillate in Table I) which has been distilled off by the steaming of the sodium salts of acid oil is 42% of acid oil, 11 of basic oil and 47 of neutral oil; the absorption diminutions of this neutral oil by 80 and 98% sulfuric acid are 51.5 and 44.0 % respectively. Thus the portion unabsorbed by 98% sulfuric acid is only 4.5%.

Neutral oil in the low temperature cresol No. 1 is also absorbed largely by 80 and 98% sulfuric acid, and the unabsorbed is about 2%. Therefore the neutral oil which enters into the sodium salt of the acid oil through dissolution or mingling, is such a peculiar oil as to be absorbed in 80 and 98% sulfuric acid.

Basic oil forms particular compounds with acid oil[15], and a large amount of the former is removed by sulfuric acid washing, but through dissolution its portion remains, similar to the case of the neutral oil, in the sodium salts of acid oil, forming the impurities in the normal acid oil.

On this account, not only by the above mentioned manufacturing process but also by the improved process where the sodium salts of acid oil are washed with benzene, more or less impurities, including weak acid, strong acid and neutral and even basic oil, get inevitably mixed with the low temperature cresol No. 1.

(2) **Decrease of the Impurities by Refining.**—As shown in Table VI the impurities in the refined cresol have considerably decreased in contrast to those in the low temperature cresol No. 1. According to a qualitative test the presence of catechol is indicated in the strong acid oil of the low temperature cresol No. 1, but not in the refined cresol. The iodine number of the strong acid oil in the low temperature cresol No. 1 and that of the strong acid oil in the refined cresol is 180.8 and 73.9 respectively. Diminution of iodine number seems to indicate the decrease of unsaturated acids, the content of the weak acid oil having scarcely changed.

The presence of carbonyl compounds is shown by a qualitative test in the neutral oil of the low temperature cresol No. 1, but not in the refined cresol. The iodine number of the neutral oil in the low temperature cresol No. 1 and that of the neutral oil in the refined cresol are 59.2 and 24.2 respectively, and this diminution seems to indicate the decrease of unsaturated compounds.

As to the neutral oil of the low temperature cresol No. 1 and that of the refined cresol, the absorption diminutions by 80% sulfuric acid are 24.0 and 9.4 volume % respectively; by 98% sulfuric acid they are 73.5 and 86.0%, unabsorbed part being 2.5 and 4.6%.

As the yield of the refined cresol is 90%, the decrease of the neutral oil contained in 100 cc. of the low temperature cresol No. 1 by this refining process is calculated as follows: the absorption diminution 0.176 cc. by 80% sulfuric acid is decreased to 0.035 cc., the absorption diminution 0.539 cc. by 98% sulfuric acid is decreased to 0.318 cc., and unabsorbed oil 0.018 cc. is decreased to 0.017 cc..

Since carbonyl compounds are well absorbed by 80% sulfuric acid and easily react with iodine, it may be said that carbonyl impurities are especially cut down by this refining process. Almost all basic oil is removed by this process. As shown in Table VII, the content of sulfur compounds decreases considerably by this purification.

Summary

Low temperature cresol No. 1 has an offensive smell, and its spontaneous

15) Y. Ohshima and K. Ishibashi, ibid., 29, 445 (1925).

coloration is remarkable. It was treated with an oxidizing agent and active clay for the purpose of refining, and then washed with sodium bicarbonate solution in order to remove carboxylic acids which give a strong peculiar smell. Refined cresol which has no more offensive smell and shows a little spontaneous coloration, was obtained.

The impurities in the low temperature cresol No. 1 and in the refined cresol were measured, and it was found that in the refined cresol every impurity was decreased; especially unsaturated carboxylic acids, carbonyl compounds and basic oil were diminished. In the strong acid oil were detected, propionic, *iso*-butyric, *n*-butyric, *iso*-valeric, *n*-valeric acids and catechol, in the weak acid oil, *p*-cresol, 2, 4- and 2, 5-dimethylphenols, in the neutral oil, *n*-propyl methyl ketone, mesityl oxide, *n*-amyl methyl ketone, *iso*-butyl methyl ketone, *o*-hydroxybenzaldehyde, benzaldehyde, 4-methylcyclohexanone, acetophenone, *p*-xylene, mesitylene and naphthalene and in the basic oil, 2-, 3-, 4-methylpyridines, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-dimethylpyridines, 4-ethylpyridine and 2,4,6--trimethylpyridine, respectively.

Sulfur compounds were measured in accordance with chemical forms, and it was found that free sulfur and mercaptans are contained as the predominant components, and alkyl disulfides as the next; a little hydrogen sulfide, alkyl sulfides and thiophenes are also present.

Coal tar contains many components, and two hundred and eighty-two[16], or three hundred and ninety-four components[17] have already been reported in the literature of the subject.

But *n*-propyl methyl ketone, mesityl oxide, *n*-amyl methyl ketone, *iso*-butyl methyl ketone, *o*-hydroxybenzaldehyde, benzaldehyde and 4-methylcyclohexanone, that have been identified in this study, are not found in literature. Among those substances listed above, many have strong peculiar smell, and exhibit spontaneous coloration.

The refined cresol, which was treated with the oxidizing agent, active clay and sodium bicarbonate solution, scarcely has any offensive smell and exhibits only a slight spontaneous coloration. Measurement of the impurities in the refined cresol shows that almost all the above mentioned substances have been removed. Thus it is concluded that an offensive smell and spontaneous coloration of the low temperature cresol No. 1 arise, at least partially, from these substances.

The author wishes to express his sincerest gratitude to Dr. K. Ohyama of Ube Industries, Ltd., Dr. B. Masumoto and Dr. T. Matsuura of Hiroshima University for their kind and constant guidance in the course of this work and also to Mr. M. Kishida, Mr. S. Nagai, Mr. S. Mori, Mr. Y. Kawaguchi and others of Ube Industries, Ltd. for their kind assistance.

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16) O. Krubber, A. Raeithel and G. Grigoleit, *Erdöl und Kohle*, **8**, 637 (1955).

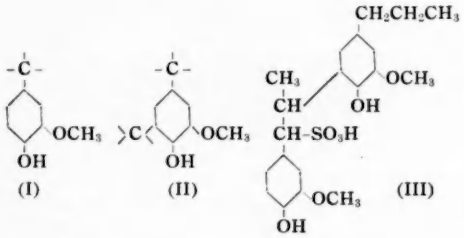
17) The Coal Data Book (Loose-Leaf), Section A-4 "List of compounds identified in and isolated from coal tar", The Coal Tar Research Association, Oxford Road, Gomersal, Nr. Leeds. (1956).

On the Cooking Mechanism of Wood. XVII. Further Investigations on the Conductometric Titrations of Lignin Models with Phenolic Hydroxyl Groups and a Brief Theory of the Conductometric Titration of Phenols

By Hiroshi MIKAWA and Koichiro SATO

(Received March 4, 1958)

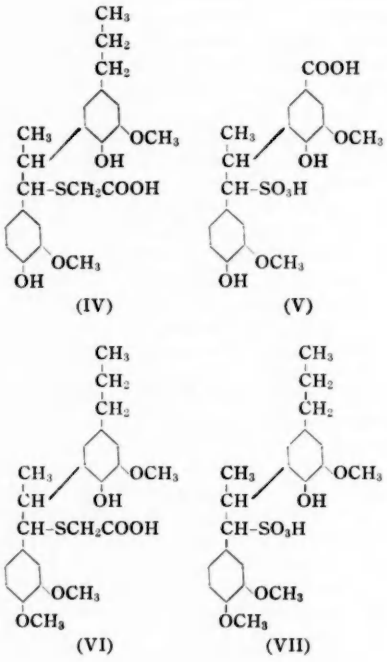
Conductometrically Untitratable *o*-Substituted Phenolic Hydroxyl Group.— In part XIII of this series[1], it was reported that although simple guaiacol-type phenolic hydroxyl group (I) was conductometrically titratable, having a very clear "break" (the neutralization point), non-guaiacyl phenolic hydroxyl group of the model sulfonic acid (III) was conductometrically untitratable. Assuming in general that the phenolic hydroxyl groups belonging to type-II are conductometrically untitratable, a method of the separate estimation of both type-I and -II phenolic hydroxyl groups of lignosulfonic acid was wroked out with the aid of the ultraviolet absorption spectra taken simultaneously with the conductometric titration. It seems, therefore, to be quite important to make further confirmation of the non-titratability of such phenolic hydroxyl group, with other model compounds.



(I) (II) (III)

Four model compounds IV-VII, all containing type-II phenolic hydroxyl groups, were therefore conductometrically titrated and it was confirmed that such phenolic hydroxyl groups were not conductometrically titratable.

As shown in Figs.1—3, conductometrically titratable groups of the model compound IV are its carboxyl group and one of its two phenolic hydroxyl groups, one phenolic hydroxyl, possibly that of type II, remaining untitrated.



(IV) (V) (VI) (VII)

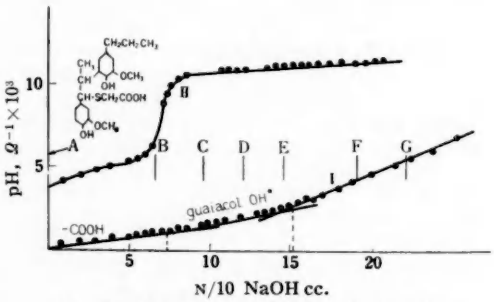


Fig. 1. Conductometric(I) and potentiometric(II) titrations of the model compound IV.

1) H. Mikawa, K. Sato, C. Takasaki and K. Ebisawa, This Bulletin **29**, 245 (1956).

Fig. 4 shows that the titratable groups of the model compound V are as expected the sulfonic acid group, the carboxyl group and only one of its two phenolic hydroxyl groups, the ratio of the strongly acidic part and the weakly acidic part of the titration curve being 1:2. No perceptible "break" existed in the weakly

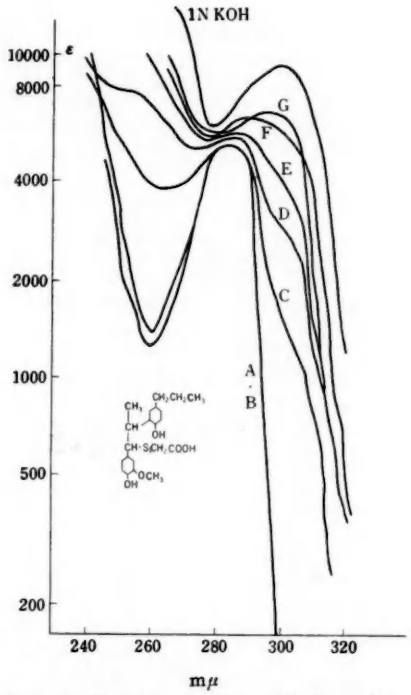


Fig. 2. Change of the UV-absorption spectrum observed during the titration of the compound IV.

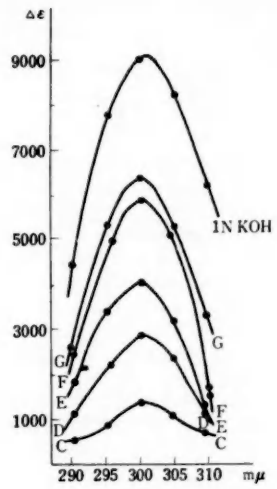


Fig. 3. $\Delta\varepsilon$-curves obtained at point C—G of the conductmetric titration curve of the compound IV shown in Figs. 1 and 2.

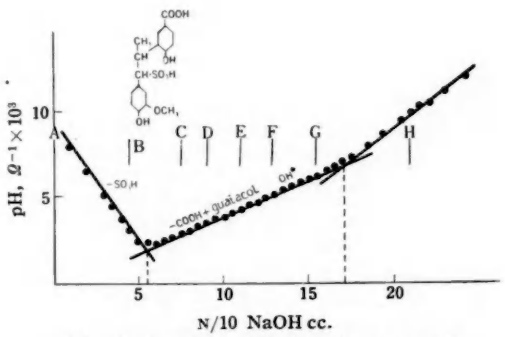


Fig. 4. Conductmetric titration curve of model compound V.

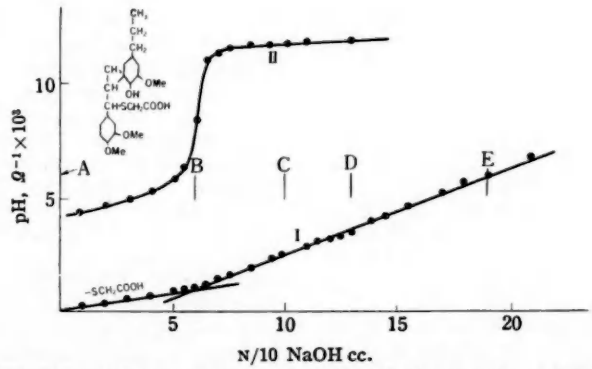


Fig. 5. Conductmetric(I) and potentiometric(II) titrations of the model compound VI.

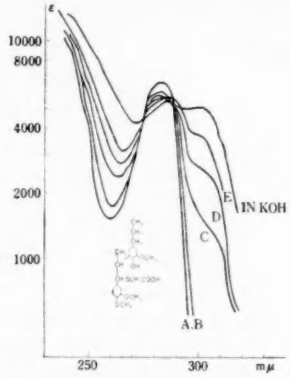


Fig. 6. Change of the UV-absorption spectrum observed during the titration of the compound VI.

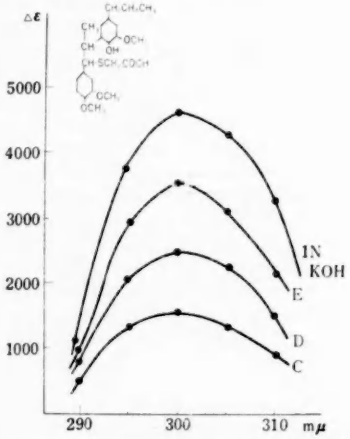


Fig. 7. $\Delta\varepsilon$-curves obtained at point C~E of the conductometric titration curve of the compound VI shown in Figs. 5 and 6.

acidic part just as in the case of lignosulfonic acid. Thus, the separation of carboxyl group and the conductometrically-titratable phenolic hydroxyl group seems to be impossible even in the case of the model compound.

Model compound VI demonstrates, as shown in Figs. 5—7, most clearly that type-II phenolic hydroxyl group is not conductometrically titratable. The titratable group is only its carboxyl group in this case, type-II phenolic hydroxyl of this compound having no effect on the titration curve.

The same is true again in the case of the model compound VII, as shown in Figs. 8—9. Type-II phenolic hydroxyl of this

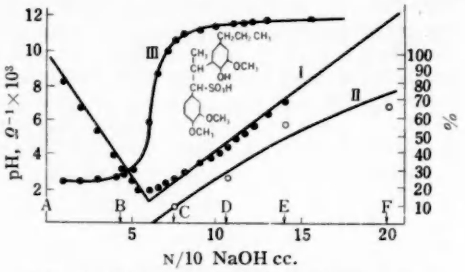


Fig. 8. Conductometric(I) and potentiometric(III) titrations of the model compound VII and the percentage of the phenolic hydroxyl group ionized during the titration (II).

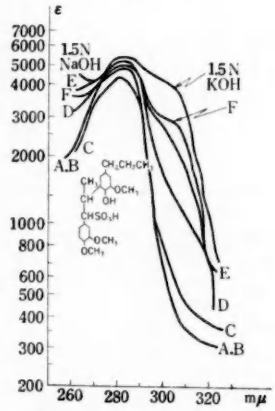


Fig. 9. Change of the UV-absorption curve observed during the titration of the compound VII shown in Fig. 8.

compound was not titrated.

From the above findings it will now safely be concluded that type-II phenolic hydroxyl group of at least III-VII type may be in general definitely conductometrically untitratable. A method of the separate estimation of both type I and type II phenolic hydroxyl groups, worked out in the previous communication, may therefore be valid in general.

Conductometric Titration of *o*, *o'*-Diphenol-Type Phenolic Hydroxyl Groups.—We have now considerable accumulation of the facts supporting the existence of *o*, *o'*-diphenol type phenolic hydroxyl groups in lignin. Among others according to the recent view of the biosynthesis of lignin, the formation of such *o*, *o'*-diphenol type linkage is expected during the dehydrogenative condensation of coniferyl alcohol or other monomeric

phenolic lignin precursors[2], as the phenols, without double bond conjugated with benzene nucleus in its para position, dimerize easily resulting in the formation of *o*, *o'*-diphenol structure by dehydrogenation[3]. The results of the nitrobenzene oxidation of lignin and lignin-model compounds support also the existence of such structure in lignin, as degradation products having such *o*, *o'*-diphenol-type linkage are obtained only from lignin but not from model compounds with simple guaiacol type nucleus[4,5].

Three water-soluble model compounds VIII—X were prepared and titrated conductometrically and the results are summarized in Fig. 10.

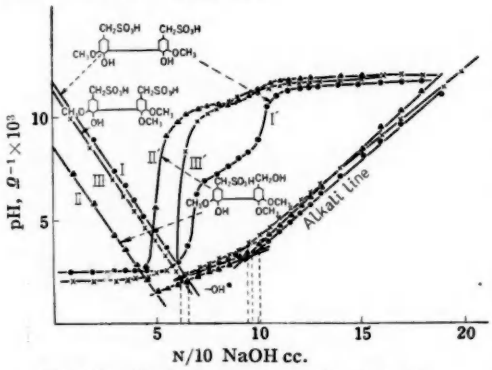
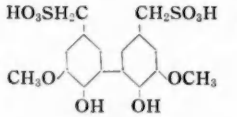
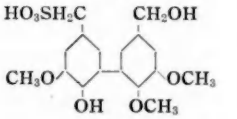


Fig. 10. Conductometric and potentiometric titrations of the model compounds VIII—X.

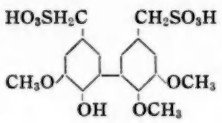
Only one of the two phenolic hydroxyl groups of the compound VIII was found to be titratable as shown by curves I and I′ of the same figure. Phenolic hydroxyl groups of the compounds IX and X were conductometrically titratable (cf. curves II, II′; III and III′). That the phenolic hydroxyl group of the compound XI was conductometrically titratable by back titration in aqueous alcohol solution, as it was already reported in part XIII of this series[1].



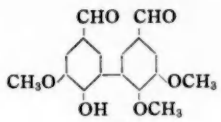
(VIII)



(IX)



(X)



(XI)

According to G. Aulin-Erdtman one of the phenolic hydroxyl groups, which belong to *o*, *o'*-diphenol is very strongs, on the other hand, the remaining one is extremely weak[6]. It has been assumed that, owing to the formation of hydrogen bonding between two hydroxyl groups, a proton belonging to any one of these two hydroxyl groups acquires very strong tendency for ionization, although the remaining one is held firmly by net negative charge left after the ionization of one phenolic hydroxyl group, resulting in weakening of the acidity of this second hydroxyl group. As the phenolic hydroxyl groups of monomethyl ethers IX—XI are conductometrically titratable, there seems to exist no strong hydrogen bonding between phenolic hydroxyl group and methoxyl group in these structures.

We shall now be able to summarize the limitations of our method of the separate estimation of type-I and II phenolic hydroxyl groups as follows. If lignosulfonic acid contains *o*, *o'*-diphenol type structure or its monoether structure like those of VIII—XI, (i) one phenolic hydroxyl group may be estimated per such structure as conductometrically titratable type-I hydroxyl group; (ii) one very weak phenolic hydroxyl group of *o*, *o'*-diphenol structure will be missed completely in so far as the total amount of phenolic hydroxyl groups is estimated spectroscopically. The type-I phenolic hydroxyl group estimated by our method may, therefore, contain half of the phenolic hydroxyl groups belonging to *o*, *o'*-diphenol structure and that belonging to *o*, *o'*-diphenol monoether structure if any.

Brief Theory of the Conductometric Titration of Very Weak Phenols.—As stated above, the behavior of type-I and II phenolic hydroxyl groups in conductometric titration is very different, the former being titratable while the latter is completely untitratable. As it is easily expected that the difference between the two types of phenols is due to the difference of dissociation constants of both types of phenolic hydroxyl groups, it

2) K. Freudenberg and Hubner, *Chem. Ber.*, **85**, 1181 (1952).
K. Freudenberg and H. Dietrich, ibid, **86**, 4 (1953).
K. Freudenberg and W. Fuche, ibid., **87**, 1824(1954).
3) H. Erdtman, *Biochem. Z.*, **258**, 172 (1933).
4) I. A. Pearl, *J. Am. Chem. Soc.*, **72**, 2309 (1950).
5) J. C. Pew, ibid., **77**, 2831 (1955).
6) G. Aulin-Erdtman, *Svensk Papperstid.*, **57**, 745 (1954).

must be interesting to make a brief theoretical discussion on the conductometric titration of phenols having different dissociation constants.

Assume that a strong base BOH is added to a solution of a weak acid (phenol) HA of concentration [S] and the total volume of the solution remains constant. Applying the mass law to the dissociation of the acid:

$$[H^+] = K_a[HA]/[A^-] \quad (1)$$

where K_a is the dissociation constant of the acid HA. From the principle of electroneutrality of the solution it follows that:

$$[A^-] + [OH^-] = [B^+] + [H^+] \quad (2)$$

Since the total amount of the acid HA used is [S]:

$$[HA] = [S] - [A^-] \quad (3)$$

Substituting 2 and 3 into 1 to eliminate both $[A^-]$ and [HA], one finds that:

$$[H^+] = K_a \frac{1 - [\alpha_t + ([H^+] - [OH^-])/[S]]}{\alpha_t + ([H^+] - [OH^-])/[S]} \quad (4)$$

where $\alpha_t = [B^+]/[S]$ represents the ratio of the amount of the added base BOH to the total amount of the acid. Since the pH of the solution is in alkaline side throughout the titration, the hydrogen ion concentration is negligibly small in comparison to that of hydroxyl ion:

$$[H^+] \ll [OH^-]$$

Hence from equation 4 it follows that:

$$[H^+] = K_a\left[1 - \alpha_t + \frac{[OH^-]}{[S]}\right] \Big/ \left[\alpha_t - \frac{[OH^-]}{[S]}\right] \quad (5)$$

Eliminating $[H^+]$ by using ion-product of water $K_w = [H^+][OH^-]$, $[OH^-]$ can be calculated:

$$[OH^-] = -\frac{1}{2}\left[\left([S] - [S]\alpha_t - \frac{K_w}{K_a}\right) + \sqrt{\left([S] - [S]\alpha_t - \frac{K_w}{K_a}\right)^2 - 4\frac{K_w}{K_a}[S]\alpha_t}\right]$$

This equation gives the concentration of hydroxide ion $[OH^-]$ of the solution of weak acid HA of concentration [S] when titrated with strong base BOH until α_t of the equivalent point. When the concentration [S] is assumed to be 0.01 normal, the concentration of the hydroxide ion increases during the titration for phenols having different pK values 9 to 12, as shown in Fig. 11.

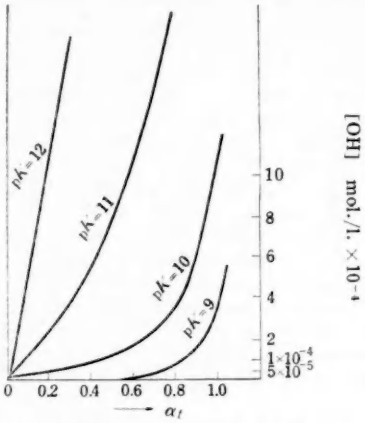


Fig. 11. The increase of the concentration of the hydroxide ion during the titration of phenols having various pK values.

Next, the specific conductivity of this solution is the summation of the products of the mobilities and one thousandth of the concentrations of the ions, as the concentration is expressed by mol./liter, that is

$$\kappa \cdot 10^3 = L_{H^+}[H^+] + L_{OH^-}[OH^-] + L_{A^-}[A^-] + L_{B^+}[B^+] \quad (6)$$

where L_{H^+}, L_{OH^-}.....are the mobilities of the ions. As L_{H^+} and L_{OH^-} are of the same order of magnitude and $[H^+] \ll [OH^-]$, $L_{H^+}[H^+]$ is negligible when compared to $L_{OH^-}[OH^-]$. Although of course $[A^-]$ and $[B^+]$ are not equal because of the hydrolysis, for simplicity we may be able to assume $[A^-] \fallingdotseq [B^+]$, as the value of L_{A^-} is, as expected, not very large. Then

$$\kappa \cdot 10^3 = L_{OH^-}[OH^-] + (L_{A^-} + L_{B^+})0.01\alpha_t$$

Here, $L_{OH^-} = 174$ and $L_{Na^+} = 43$. The value of L_{A^-} is of course not known but as the mobility of large organic anion is not expected to be so large as that of, for example, sodium ion, L_{A^-} is assumed for simplicity to be 10 in the above equation. Then,

$$\kappa \cdot 10^3 \fallingdotseq 174[OH^-] + 0.53\alpha_t \quad (7)$$

This equation 7 represents the conductometric titration curve. It is clearly shown that because of hydrolysis the measured conductivity lies higher by $174[OH^-]$ over the salt line $0.53\alpha_t$. Relations between κ and α_t calculated for various pK phenols having different pK values are shown in Fig. 12.

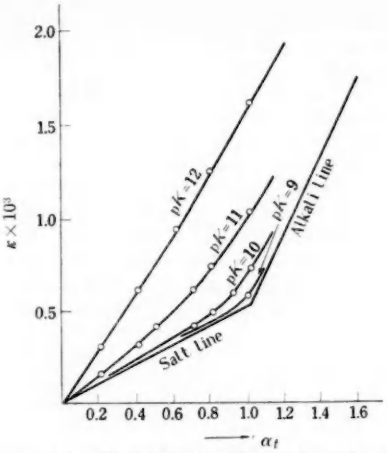


Fig. 12. Theoretically obtained conductometric titration curves of phenols having various pK values.

It is clearly demonstrated in this figure that one can calculate the equivalent point in so far as the pK values of the acids are smaller than 10, it being however quite impossible to find out the equivalent point when pK values are larger than 10. The difference of only about one unit in the pK values near pK 9~11 definitely decide whether the phenol in question is conductometrically titratable or not. As the calculated titration curve for pK 12 is nearly linear, it is expected that the pK value of phenolic hydroxyl group of type II may be 12 or larger.

Experimental

Model Compounds IV, V and VI.—Compounds IV and VI were synthesized as reported previously[7]. Compound V was prepared according to Richtzenhain[8]. The sulfonic acid was separated as its benzylthiuronium salt was not crystallizable.

Anal. Found: C, 54.14; H, 5.58. Calcd. for $C_{26}H_{30}O_9N_2S_2$: C, 54.08; H, 5.58%.

Synthesis of α-(3,4-Dimethoxyphenyl)-β-(2-hydroxy-3-methoxy-5-propylphenyl)-*n*-propanesulfonic Acid (VII).—Dihydrodehydro-di-isoeugenol methyl ether (5 g.) was dissolved in 500 ml. of cooking acid (to 25 g. of sodium hydroxide in one liter of 50% alcohol was added 30 g. of sulfur dioxide after having been neutralized to pH 6 with sulfur dioxide) and heated in a vigorously rotating stainless autoclave for 20 hours at 135°C with a little amount of copper powder. After filtration, excessive sulfur dioxide was expelled in vacuo, sulfuric acid added, sulfur dioxide expelled and the solution was set aside over-night in order to decompose thiosulfate if any, after having adjusted the concentration of excess sulfuric acid to one normal. Sodium was removed by ion exchange, and the solution was concentrated, neutralized with barium carbonate, filtered, concentrated to dryness and extracted with water. A concentrated solution of benzylthiuronium hydrochloride was added to the extract thus obtained and the viscous precipitate of benzylthiuronium salt was washed with water, dissolved in a little amount of alcohol and reprecipitated with water. After having been purified twice by reprecipitation, the precipitate was rubbed with ice water. The powder thus obtained was not crystallizable.

Anal. Found: C, 58.98; H, 6.51; N, 5.11. Calcd. for $C_{29}H_{38}O_7N_2S_2$: C, 58.9; H, 6.49; N, 4.75%.

As the material was not obtained as crystals, the analytical values obtained did not agree well with the calculated values. Conductometrically the sulfonic acid group amounted to 92.5% of the theoretical amount. Without further purification the material was used for our purpose.

Synthesis of Dehydro-divanillyl Sulfonic Acid (VIII).—Although this compound is already known[9], no details are published as yet. Dehydro-divanillin was synthesized according to Elbs and Lerch[10]. It was found that dehydro-divanillin was very easily purified via its mono sodium salt. The crude product was dissolved in hot sodium hydroxide solution, which, upon cooling, separates beautiful crystals of mono sodium salt, which was recrystallized from aqueous alcohol.

Anal. Found: C, 59.21; H, 4.54; Na, 6.83. Calcd. for $C_{16}H_{13}O_6Na$: C, 59.3; H, 4.08; Na, 7.10%.

Dehydro-divanillin was dissolved in the least amount of dilute alkali, reduced with an exess of sodium borohydride until free from aldehyde color-reaction, acidified with carbon dioxide and the separated crystalline dehydro-divanillyl alcohol was filtered, m. p. 190°C.

Anal. Found: C, 62.51; H, 6.06; OCH_3, 20.32. Calcd. for $C_{16}H_{18}O_6$: C, 62.8; H, 5.89; OCH_3, 20.26%.

Dehydro-divanillyl alcohol thus obtained (2 g.) was shaken at 100°C for two hours in a sodium-base sulfite cooking acid of pH 1.8 (100 ml.). Dehydro-divanillyl sulfonic acid was separated as barium salt just as in the case of vanillyl sulfonic acid.

Anal. Found: C, 31.54; H, 3.58; S, 10.5; Ba, 22.42; OCH_3, 10.69. Calcd. for $C_{16}H_{19}O_{10}S_2Ba$: C, 33.7; H, 2.81; S, 11.2; Ba, 24.1; OCH_3, 10.69%.

Synthesis of Dehydro-divanillyl Alcohol Monomethyl Ether. Monosulfonic Acid (IX) and Disulfonic Acid (X) of the Monoether.—Dehydro-divanillin monomethyl ether[1]

7) H. Mikawa et al., This Bulletin, **29**, 245 (1956).
8) Richtzenhain and Alfredsson, *Acta Chem. Scand.*, **8**, 1519 (1954).
9) E. Adler and S. Hernestam, ibid., **9**, 319 (1955).
10) K. Hlbs and H. Lerch, *J. prakt. Chem.*, **93**, 1 (1916).

was dissolved in a calculated amount of sodium hydroxide, reduced with excessive sodium boronhydride over-night until free from aldehyde color-reaction, neutralized with diluted hydrochloric acid and extracted exhaustively with chloroform. The oily product thus obtained in nearly theoretical yield was not crystallizable.

The oily dehydro-divanillyl alcohol monomethyl ether obtained was sulfonated at pH 1.9 for four hours at 100°C by sodium-base sulfite cooking acid. The crystalline barium salt separated as usual was not analyzed, however the strong acidic group amounting to 112% of the sulfonic acid group calculated from the formula IX was conductometrically titrated. This crystalline barium salt may, therefore, be contaminated a little by disulfonic acid X.

In order to prepare disulfonic acid X dehydro-divanillyl monomethyl ether was sulfonated at 135°C for five hours with the same cooking acid as above. As usual the disulfonic acid was isolated as barium salt. Conductometric titration of the acid revealed the existence of a strong acidic group amounting to 98.8% of the calculated amount.

Summary

1. Conductometric titrations of the model compounds IV, V, VI and VII provided reconfirmation of the previously reported[1] findings that simple guaiacol-type phenolic hydroxyl group I was conductometrically titratable, while non-guaiacyl phenolic hydroxyl group belonging to type II was conductometrically untitratable.

2. It was thus further confirmed, that the separate estimation of both type-I and -II phenolic hydroxyl groups of lignosulfonic acid by the method of conductometric titration is possible in combination with the ultraviolet absorption spectra taken simultaneously with the conductometric titration without any dilution of the solution.

3. As we have now considerable accumulation of facts supporting the existence of *o*, *o'*-diphenol type phenolic hydroxyl group in lignin, three water-soluble model compounds VIII, IX and X were titrated conductometrically. Phenolic hydroxyl groups of IX and X were found to be conductometrically titratable. Of the two phenolic hydroxyl groups of the model compound VIII only one was found to be titratable.

4. A brief theoretical consideration of the conductometric titration of extremely weak acid (phenol) having pK values larger than 9 were made. As is evident from Fig. 12, which shows theoretical conductometric titration curves of phenols having pK values 9~12, one can calculate the equivalence-point in so far as the pK values of the phenols are smaller than 10; it is, however, impossible to find the equivalence-point when pK values are larger than 10. As the calculated titration curve for pK 12 is nearly linear, it is expected that the pK value of phenolic hydroxyl group of type II is 12 or larger.

The authors wish to express their gratitude to Dr. H. Okada, the head of the laboratory, and Miss S. Suehiro for their encouragement.

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Capture of Radioactive Cesium onto a Phosphomolybdate Precipitate Layer and its Determination

By Tadashi HARA

(Received January 28, 1958)

The object of this research was to find a simple, rapid and accurate method for the determination of radioactive cesium in solutions which are extremely dilute or contain various substances. In the conventional method[1] for the determination of radioactive cesium, the coprecipitation method using a suitable carrier has been mainly adopted. However, that method is incomplete and unsuitable for such sample solutions as mentioned above.

Therefore, a new method is here presented which is based on filtering a sample solution through a precipitate layer of thallium phosphomolybdate and directly measuring the radioactivity of the precipitate on the layer after washing and drying. In this method, the coexistence of various substances scarcely ever interferes with the determination of radioactive cesium and moreover the cesium, even in 2 liters of a solution, is almost completely recovered.

Experimental

Apparatus and Chemicals. — The Shimadzu D-55 type GM-counter, a specially designed glass-filter and a holder as indicated in Fig. 1 were used for the measurement of the radioactivity. Phosphomolybdic acid was prepared by Brauer's method[2] and a 2% solution in 2% nitric acid was used. The thallium solution which contained 1 mg. thallium per 1 ml. of 2% nitric acid was prepared by dissolving metallic thallium in nitric acid. Sodium cobaltinitrite reagent was prepared by Ishibashi's method[3]. Processed cesium-137, thallium-204 and strontium-90 were obtained and diluted to about 1 μC/ml.

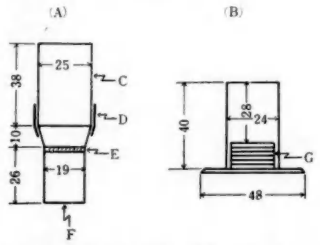

Fig. 1. Glass-filter and holder (unit; mm.)
(A) Glass-filter, separable to C and F
(B) Holder
C; Glass-cylinder
D; Gum
E; Filter-plate
F; Glass-filter, used for the measurement of radioactivity
G; Metallic-plates

Procedure.—Fifty ml. of thallium solution, 4 ml. of concentrated nitric acid and 126 ml. of water were placed in a 300 ml. beaker. Then, 20 ml. of phosphomolybdic acid was added to it. After being concentrated to about 7 ml., the contents were transferred into a glass-filter as shown in Fig. 1, filtered and washed with 2% nitric acid. The washing was continued until only a small amount of washing solution remained on the precipitate layer. Then, the sample solution which was a 2% nitric acid solution containing radioactive cesium was filtered through the previous glass-filter at the rate of 2 drops every 3 seconds or more. At the end of the filteration, the precipitate layer was washed with 2% nitric acid followed by concentrated acetic acid and dried at 120°C for about an hour. Finally, the activity on the precipitate layer was measured by using a holder as shown in Fig. 1 and GM-counter.

Results and Discussion

Reproducibility.—The results obtained

TABLE I
REPRODUCIBILITY OF MEASUREMENTS

No. of sample	Counts per min.
1	3017
2	3032
3	2928
4	2975
5	3071
6	3033
7	2957

Mean value=3002
Max. error=+2.5%

1) For example, B. Kahn, D. K. Smith and C. P. Straub, *Anal. Chem.*, **29**, 1210 (1957).

2) G. Brauer, "Handbuch der Präparativen Anorganishen Chemie", Ferdinand Enke Verlag, Stuttgart (1954), p. 1278.

3) M. Ishibashi, "Qualitative Analysis", Shōkabō, Tōkyo (1947), p. 25.

with regard to seven samples are shown in Table I. The values for each sample correlate within an error of ±2.5%. Therefore it is believed that the present method can be used adequately for the quantitative determination of radioactive cesium.

Proportionality. — Portions of 0.2, 0.5, 0.8, 1.1, 1.4, 1.7, 2.0 and 2.5 ml. of each radioactive cesium solution were diluted to a 100 ml. of 2% nitric acid solution with nitric acid and water. The results obtained with these samples are indicated in Fig. 2. It is clear that a linear relationship holds between the amount of radioactive cesium in a sample solution and the strength of the activity on the precipitate layer, and the maximum error involved is 8.3% when this calibration curve is used.

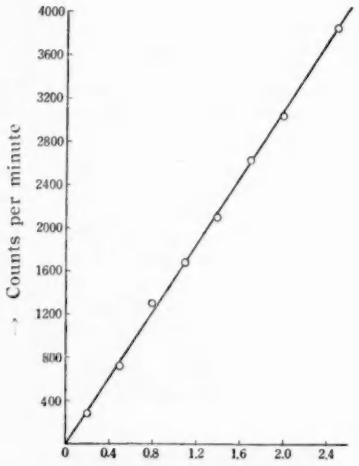

Fig. 2. Calibration curve

Volume of Sample Solution.—Portions of 25, 50, 100, 400, 600, 1000 and 2000 ml. of each sample solution were used in a 2% nitric acid solution which contained about 1 μC of cesium. The results in Table II indicate that the recovery of radioactive cesium is almost complete. Therefore, all the sample solutions in the following experiments will be diluted to 100 ml.

TABLE II
VOLUME OF SAMPLE SOLUTIONS

Volume (ml.)	Counts per min.
25	2974
50	3051
100	2962
400	2985
600	2958
1000	2974
2000	2992

Amount of the Precipitate.—Table III shows the relationship between the amount of the precipitate and the activity of the precipitate for the case where a definite amount of radioactive cesium is used. It is seen from the table that the activity gradually increases in accordance with an increasing amount of the precipitate. Therefore, the amount of the precipitate had better be as definite as possible for accurate measurements.

TABLE III
AMOUNTS OF THE PRECIPITATE

Tl soln. (ml.)	Wt. of ppt. (mg.)	Counts per min.
2	13.6	2548
5	25.8	2669
10	39.5	2712
20	69.1	2762
30	90.5	2849
50	156.7	2986
75	204.3	3113
100	275.0	3123

Concentration of Nitric Acid. — The relationship between the concentration of nitric acid in the sample solution and the activity of the precipitate is shown in Table 4. The data indicate that the activity slowly increases with an increase in the concentration of the nitric acid. However for convenience and economy, in view of the small difference all sample solution were prepared as 2% nitric acid solution.

TABLE IV
CONCENTRATION OF NITRIC ACID IN SAMPLE SOLUTIONS

Concn. of HNO_3 (%)	Counts per min.
0.0	2917
0.5	2957
1.0	2945
2.0	2967
4.0	3013
8.0	3068
16.0	3113

Rate of Filtration. — The relationship between the rate of filtration and the activity of the precipitate is shown in Table V. The results indicate that radioactive cesium is completely captured on

the precipitate, when 100 ml. of sample solution is passed as uniformly as possible through the precipitate layer for more than 27 minutes.

TABLE V
VELOCITY OF FILTRATION

Time (min.)	Counts per min.
8	2812
18	2937
27	2997
60	3013
120	3058

Capturing Capacity of Cesium on the Precipitate.—This experiment was made to determine what amount of cesium is captured on a definite amount of the precipitate. The results obtained are shown in Table VI and indicate that an amount of cesium chloride less than 500 μg. is almost completely captured on about 156 mg. of thallium phosphomolybdate.

TABLE VI
CAPTURING CAPACITY OF CESIUM ON THE PRECIPITATE

CsCl taken g.	Activity (cpm)		Wt. of ppt. mg.
	Ppt.	Filt.	
5	3017	0	—
10	2997	0	—
25	3091	0	—
50	3021	0	—
100	3059	0	—
200	2978	0	—
500	3085	0	—
1000	2856	0	157.3
2000	2514	11	157.5
5000	1710	368	156.3
10000	1068	1228	155.4

The radioactive cesium in the filtrate was determined by the cobaltinitrite method using potassium as a carrier. The results obtained in the preliminary experiment are shown in Table VII.

TABLE VII
PRELIMINARY EXPERIMENT BY COBALTINITRITE METHOD

Cesium-137 soln.	K_2SO_4 taken	Counts per min.
0.5 ml.	20 mg.	608
1.0 〃	〃	1206
2.0 〃	〃	2393

Distribution of Cesium on the Precipitate Layer. — This experiment was made to determine how the radioactive cesium was distributed on the precipitate layer. Three different procedures were tested with the same amount of radioactive cesium and the results obtained are shown in Table VIII.

TABLE VIII
DISTRIBUTION OF CESIUM ON THE PRECIPITATE LAYER

Exp. No.	Counts per min.
1	2381
2	3061
3	2405

Exp. 1; Cesium-137 was coprecipitated with thallium phosphomolybdate.
Exp. 2; The present method.
Exp. 3; The precipitate followed by the present method was homogenized.

Judging from the self-absorption by the precipitate and the results indicated in Table VIII, it is inferred that the radioactive cesium dose not uniformly distribute itself in the precipitate layer, but is captured more in the upper layer than in the lower of the precipitate. Moreover, a measurment of the activity by the present method is more sensitive than that by the coprecipitation method. Therefore, the present method is superior to the conventional coprecipitation method.

Solubility of the Precipitate. — This experiment was made to investigate how much precipitate is dissolved when 100 ml. of 2% nitric acid solution is passed through the precipitate layer. The solubility was radiometrically determined by the use of radioactive thallium-204 as a tracer. The results obtained are shown in Table IX and the solubility was found to be 0.18 mg. per 100 ml. of the filtrate at 20.5°C.

TABLE IX
SOLUBILITY OF THE PRECIPITATE

	Ppt. layer	100 ml. of filt.
Wt.	157.6 mg.	?*
cpm	9630	11

* Thallium-204 in the filtrate was precipitated by using the same amount of thallium as that in the precipitate layer.

Mechanism of Cesium Capturing.—These experiments were made to clarify the mechanism by which cesium was captured on the precipitate. 1.47×10^{-4} moles of thallium phosphomolybdate labelled with radioactive thallium-204 was used as the precipitate layer and potassium, rubidium and cesium chloride solution each of which contained 2.94×10^{-4}

moles in 100 ml. of 2% nitric acid, were used as sample solutions, After a sample solution is filtered through the precipitate layer, the radioactive thallium in the filtrate was coprecipitated by adding 25 ml. of 4% potassium iodide solution and 10 ml. of the standard thallium solution to it. Then the radioactivity of the precipitate was measured after filtration, washing and drying. Judging from the results shown in Table X and the other results obtained previously, the radioactive cesium in a sample solution seems to be captured by means of the ion exchange phenomenon. However it is not possible to conclude that all the cesium captured on the precipitate layer depends upon the ion exchange phenomenon.

TABLE X
MECHANISM OF CESIUM CAPTURING

Sample soln.	Radioactivity (cpm)	
	Ppt. layer	filt.
Blank	9454	11
K^+	9457	12
Rb^+	9228	349
Cs^+	8919	590

Influence of Potassium Sulfate. — The relationship between the amount of potassium sulfate and the strength of the activity is shown in Table XI. It is found that less than 1 g. of potassium sulfate in 100 ml. solution does not affect the strength of the activity on the precipitate layer.

TABLE XI
INFLUENCE OF THE POTASSIUM ION

K_2SO_4 (g./100 ml.)	Counts per min.
0.2	3068
0.5	3044
1.0	2974
2.0	2891
4.0	2751
8.0	2518
ca. 12 (Sat. soln.)	1862

Influence of Ammonium Chloride.—The relationship between the amount of ammonium chloride and the intensity of the activity is shown in Table XII. From

TABLE XII
INFLUENCE OF THE AMMONIUM ION

NH_4Cl (g./100 ml.)	Counts per min.
0.1	3008
0.2	2986
0.4	2776
0.8	2448
1.2	2011
2.5	1366
5.0	683

TABLE XIII
INFLUENCE OF THE RUBIDIUM ION

RbCl (mg./100 ml.)	Counts per min.
1	3059
2	3015
4	3016
8	2935
16	2868
32	2561
64	2228

TABLE XIV

Compounds	Wt./100 ml.	Counts per min.
LiCl	2 g.	2984
Na_2SO_4	2 〃	3017
〃	5 〃	2857
$Mg(NO_3)_2$	5 〃	3014
$CaCl_2$	5 〃	3008
$Sr(NO_3)_2$	5 〃	3013
$Ba(NO_3)_2$	5 〃	3008
$Al(NO_3)_3$	5 〃	2889
$Cu(NO_3)_2$	1 〃	2996
$AgNO_3$	1 〃	3017
$Zn(NO_3)_2$	1 〃	3045
$Cd(NO_3)_2$	1 〃	2970
$Hg(NO_3)_2$	1 〃	2999
H_3BO_3	1 〃	3020
$Pb(NO_3)_2$	1 〃	2951
$Fe(NO_3)_3$	1 〃	2912
$Co(NO_3)_2$	1 〃	3081
$Ni(NO_3)_2$	1 〃	2968
NaH_2PO_4	1 〃	3030
$Bi(NO_3)_3$	1 〃	2976
$SnCl_4$	1 〃	3052
$Cr(NO_3)_3$	1 〃	2847
Na_2WO_4	1 〃	1361
$Mn(NO_3)_2$	1 〃	2930
$Th(NO_3)_4$	0.5 〃	3008
$P_2O_5 \cdot 18MoO_3 \cdot aq$	0.5 〃	2985
NaCl	1 〃	3092
KBr	1 〃	3088
KI	1 〃	3075
K_2CrO_4	1 〃	3015
Na_2SO_3	1 〃	2962
$KClO_3$	1 〃	2920
$NaNO_2$	1 〃	1677
$H_2C_2O_4$	1 〃	3058
conc. HCl	5 ml.	2992
conc. H_2SO_4	5 〃	2942
conc. H_3PO_4	5 〃	2969
conc. CH_3COOH	5 〃	2880
$BeSO_4$	50 mg.	2982
$TlNO_3$	2.6 〃	2939
〃	13.0 〃	1113
〃	32.5 〃	373

the table, it is seen that less than 0.2 g. of ammonium chloride in a 100 ml. solution does not affect the activity on the precipitate.

Influence of Rubidium Chloride.—The results obtained in the presence of rubidium chloride are shown in Table XIII. They indicate that less than 8 mg. of rubidium chloride in 100 ml. solution does not affect the activity on the precipitate.

Influence of Other Substances.—The results obtained in the presence of various other substances are shown in Table XIV. For the most part, the substances do not interfere with the determination of radioactive cesium, but the following substances do; thallium, sodium tungstate and sodium nitrite.

Recovery in the Presence of Other Radioactive Elements.—The rare earth nuclides used in this experiment were prepared from a fission products by Yamatera's method[4] in which the fission products were easily divided into ruthenium, cesium, strontium and the rare earth group by use of mineral acids and the ion exchange resin, Dowex-50 (×8). According to the above mentioned method, about 3% of the radioactive strontium and 11% of the radioactive rare earth nuclides were captured on the precipitate layer. However, their interference with the determination of cesium was prevented by the following pretreatment. To the sample solution which contains radioactive cesium and other nuclides were added 5 mg. of ferric iron, 10 mg. of calcium ion and 50 ml. of 1% sodium carbonate solution. After filtration the filtrate was diluted to produce 100 ml. of 2% nitric acid solution. This solution was treated by the same procedure as before.

The results obtained are shown in Table XV. As can be seen from the table, the radioactive cesium is quantitatively recovered by this method in the presence of strontium-90 and rare earth nuclides which are commonly encountered in an aged fission product.

TABLE XV
INFLUENCE OF OTHER RADIOACTIVE NUCLIDES

Sample	Counts per min.
Blank	3014
R. E. N.+Cs	2989
Sr+Cs	2919
R. E. N.+Cs+Sr	2941
F. P.	472
F. P.+Cs	3464

R. E. N.; Rare Earth Nuclides
F. P.; Fission Products

Recovery of Radioactive Cesium from Natural Waters.—This experiment was made to investigate what percentage of cesium was recovered in the case of using one liter of natural water as a sample solution. One liter each of river and sea water were acidified to produce 2% nitric acid solution and filtered through a filter-paper, Tōyō-Roshi No. 5A, after a definite amount of the radioactive cesium was added to it. The same procedure as mentioned above was followed. The results obtained are shown in Table XVI and indicate that about 93% of the radioactive cesium was recovered from one liter of either river or sea water by this method.

TABLE XVI
RECOVERY OF CESIUM-137 FROM NATURAL WATERS

Sample	Counts per min.	Recovery (%)
Blank	3069	100
River water	2842	92.6
Sea water	2864	93.3

Other Results.—In these experiments, the same glass-filters were repeatedly used, but no adverse effects resulted when they were twice boiled with 2N-aqueous ammonia and dilute nitric acid for about an hour.

Summary

(1) Up to 500 μg. cesium dissolved in less than 2 liters of solution is quantitatively captured on the precipitate layer by filtering the cesium solution through it.

(2) The activity on the precipitate is proportional to the amount of cesium-137 present in the solution and consequently, the quantity of cesium-137 is easily determined.

(3) The mechanism of capturing cesium on the precipitate layer is believed to be due to the ion exchange phenomenon.

(4) Determination of the radioactive cesium by this method is not interfered with by the presence of a large amount of various substances except rubidium, cesium, thallium, tungstate and nitrite. Radioactive strontium and rare earth elements also interfere, but their interference may be prevented by pretreatment.

4) H. Yamatera, A paper read before the 10th Annual Congress, Chem. Soc. of Japan, April, 1957.

(5) Recovery of the radioactive cesium dissolved in one liter of either river or sea water are about 93%.

The author wishes to express his deep gratitude to Professor Dr. M. Ishibashi of Kyoto University and Mr. H. Yamatera of Osaka City University for their encouragement and advice. The author also expresses his sincere thanks to Mr. K. Nishimoto of Doshisha University for his valuable assistance in this research.

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The Formic Acid Rearrangement of 2-Cyclohexyl-3-butyn-2-ol

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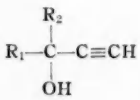
(Received April 14, 1958)

The present work, as well as the several reports from this laboratory[1,3], was directed to exploring the effect of the structure of tertiary ethynylcarbinols on the course of Rupe reaction.

Here, 2-cyclohexyl-3-butyn-2-ol (II) was chosen for another model carbinol in which R_1 (or R_2; R_1, R_2=alkyl; I) is secondary and, at the same time, R_2 (or R_1) is not primary.



(I)

It was previously shown[1] that the tertiary ethynylcarbinols may be classified into two groups in relation to Rupe reaction. One group involves the carbinols in which R_1 or R_2 is primary or secondary. They are capable of undergoing dehydration followed by hydration (at the ethynyl group), and afford chiefly ketones as the reaction product; the formation of aldehydes is generally of a small quantity.

The other group consists of the carbinols in which both R_1 and R_2 are neither primary nor secondary. They undergo mainly Meyer-Schuster rearrangement to yield aldehydes. Seemingly, the methyl group which is adjacent to the carbon atom attached to the hydroxyl group plays a role somewhat similar to the tertiary alkyl viewed from the several instances already reported[2]; the dehydration between the methyl group and the neighboring hydroxyl group seems to occur actually, however the formation of ketones is inconsiderable.

Though the carbinols such as II belong to the first group, they have only one hydrogen atom on the concerned carbon atom (adjacent to the carbon atom attached to the hydroxyl group). The question whether such a carbinol has, to a certain degree, a tendency suitable for yielding aldehydes besides ketones is now under investigation. Of course, such a trend may not necessarily result only from the above structure, however it was observed on the two model carbinols of this type. One is 3, 4-dimethyl-1-hexyn-3-ol, from the reaction products of which 3, 4-dimethyl-2-hexenal was easily isolated by simple distillation[3] (ca. 3% yield, a small but significant quantity). The other is II in the present experiment, which gave 3-cyclohexyl-2-butenal(IV) in ca. 12% yield in addition to 3-cyclohexylidene-2-butanone(III) (ca. 28% yield). That such a considerable amount of the aldehyde could easily be isolated, may be noteworthy compared with other carbinols which are capable of undergoing the usual Rupe reaction. There are of course some reports[4] regarding the isolation of aldehydes (up to ca. 10%) from the reaction products

1) T. Takeshima, *J. Sci. Research Inst.*, **45**, 211 (1951); ibid., **47**, 257 (1953); ibid., **48**, 103, 113 (1954); *J. Am. Chem. Soc.*, **75**, 4107 (1953).
2) C. D. Hurd and W. D. McPhee, ibid., **71**, 398 (1949); T. Takeshima, *J. Sci. Research Inst.*, **48**, 113 (1954).
3) T. Takeshima, *J. Am. Chem. Soc.*, **75**, 3309 (1953).
4) F. G. Fischer and K. Löwenberg, *Ann.*, **475**, 183 (1929); J. D. Chanley, *J. Am. Chem. Soc.*, **70**, 244 (1948).

TABLE I

REACTION PRODUCTS FROM II

Fraction	B. p., °C (30 mm.)	Yield, g., from 20 g. of II	Constituent
1	75~80	ca. 2.5	Cyclohexanone and possibly 3-cyclohexylidene-1-butyne
2	81~95 (81~85)*	ca. 3.2	III and possibly 3-cyclohexylidene-1-butyne
3	ca. 100~130 (ca. 105~110)*	ca. 5.5	III predominating
4	132~138 (ca. 135)*	ca. 2.3	IV

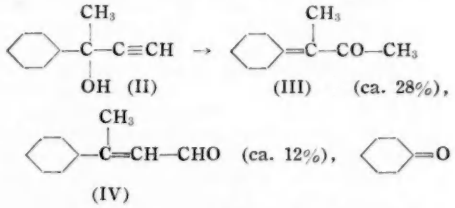
* The boiling point enclosed with parentheses shows the one at which the greater part of the fraction distilled out.

DERIVATIVES OF THE CARBONYL COMPOUNDS

Original compd.	2,4-Dinitrophenylhydrazone		Semicarbazone	
	M. p., °C	Appearance	M. p., °C	Appearance
III	123~124	Deep yellow crystals	174~175	Colorless needles
IV	199~200	Light red long plates	183~184 (slow heating) ca. 196 (rapid heating)	Colorless long plates
V	125~127	Deep yellow crystals	139~140	Colorless plates

	Dimedone Derivative	
	M. p., °C	Appearance
IV	160~161	Colorless crystals

of the carbinols which have secondary carbon atom in the concerned position.



The present experiment is outlined as follows. II was refluxed with ca. 80% formic acid and treated in the usual manner. The reaction products were distilled and four fractions were collected (consult Table I). The low-boiling fraction (fraction 1) contained a considerable amount of cyclohexanone, which, considering the fact mentioned below, seemed to owe its origin to the acid hydrolysis of III. The greater part of fraction 3 consisted of a carbonyl compound III which gave the ketonic derivatives shown in Table I. III, one of the two main products in this reaction, was practically indifferent toward Schiff reagent, had unsaturated nature, and gave pyrazoline derivative. Further, III on hydrolysis by acid gave cyclohexanone and methyl ethyl ketone as their 2,4-dinitrophenylhydrazone. Thus III proved to be 3-cyclohexylidene-2-butanone. Though the boiling point of III corresponded to the one reported by Thakur[5], the melting point of its semicarbazone was quite different from the one obtained by him.

Fraction 4, which had a pleasant smell, proved to consist of a carbonyl compound IV of formula $C_{10}H_{16}O$ of which derivatives are shown in Table I. The compound had an unsaturated aldehydic nature. On treatment with phenylhydrazine, it readily gave an oily product which had a pyrazoline reaction of a coloration different from that of III. Further, ozonolysis gave glyoxal as the 2,4-dinitrophenylosazone. Hydrogenation afforded the corresponding saturated compound V which had an intensely positive test with Schiff reagent. Thus structure IV, 3-cyclohexyl-2-butenal, and V, 3-cyclohexylbutyraldehyde, were assigned to these two compounds, respectively.

Finally, fraction 1 seemed to contain, besides cyclohexanone, a non-ketonic substance of unsaturated nature. Likewise, fraction 2, in which some quantity of cyclohexanone and III was detected as

5) R. S. Thakur, *J. Chem. Soc.*, **1933**, 1481. He obtained the ketone by a different route, and reported three melting points of somewhat indefinite nature for its semicarbazone, one distinct melting point being obtained after fractional recrystallization. The one in the present experiment was believed to be of the single compound.

their 2,4-dinitrophenylhydrazones, also contained the same substance. It was inferred from the behavior of these two fractions (see experimental part) that the compound is possibly 3-cyclohexylidene-1-butyne.

Experimental

2-Cyclohexyl-3-butyn-2-ol. — The carbinol was prepared by ethynation of acetylcyclohexane in the usual manner[1] using sodium amide as the reagent. Yield ca. 83%, b. p. 104~106° (18 mm.) (reported b. p. 106~110° (23 mm.)[6]); practically no ketonic compound was detected in this fraction by the 2,4-dinitrophenylhydrazine test. Fairly good yield could be thus obtained without depending on the liquid ammonia method[6]; in the present preparation acetylene was passed through for ca. 12 hr. at ca. −7° and the reaction mixture was then left overnight in an ice-box.

The original **acetylcyclohexane** was prepared by hydrogenating 1-acetylcyclohexene with palladium; b. p. 178~180°, yield 86%.

1-Acetylcyclohexene was prepared from 1-ethynylcyclohexanol with the aid of its acid rearrangement[7]; 130 g. of the carbinol was treated with a mixture of 12 g. of sulfuric acid, 280 g. of acetic acid and 2 g. of water. On heating, a vigorous spontaneous reaction was initiated; a large reflux condenser was preferably fitted; the heating must be stopped immediately after the initiation and the reaction, if needed, was moderated by cooling with water. The pure ketone could be obtained by this method, which contained practically no aldehyde; b. p. 110~111° (50 mm.), yield 65%.

The Formic Acid Rearrangement of 2-Cyclohexyl-3-butyn-2-ol (II). — Twenty grams of II was gently refluxed with 160 g. of ca. 80% formic acid for ca. 1 hr.; the heating was interrupted during the spontaneous boiling at the beginning. The reaction mixture was left to be cooled, and then neutralized with a concentrated solution of potassium carbonate, extracted with ether, dried by potassium carbonate, the ether driven off, and distilled collecting the following fractions. (1) b. p. 75~80° (30 mm.), ca. 2.5 g.; (2) b. p. 81~95° (30 mm.), ca. 3.2 g. (the greater part distilled out at 81~85° (30 mm.)); (3) b. p. ca. 100~130° (30 mm.), ca. 5.5 g. (ca. 28%; the greater part distilled out at ca. 105~110° (30mm.)); (4) b. p. 132~138° (30 mm.), ca. 2.3 g. (ca. 12%; the greater part distilled out at ca. 135° (30mm.)); Distillation residue, tarry material

All these fractions were colorless, scarcely soluble in water, easily soluble in common organic solvents, and had a smaller density than water at room temperature.

Fraction 1 gave considerable quantity of cyclohexanone 2,4-dinitrophenylhydrazone, which on recrystallization from hot ethanol melted at 158~160° and did not depress the melting point of an authentic sample (Found: C, 51.72; H, 5.08; N, 19.81%). Another 2,4-dinitrophenylhydrazone obtained from this fraction, perhaps that of III, was only of a small quantity; it was difficult to obtain any derivative from the same fraction by treating it, as it is, with semicarbazide reagent. It, as it is or as the ethanolic solution, readily decolorized bromine water; II apparently had much more inertia toward this reaction, and had a much higher boiling point than this fraction. Further, it gave some precipitates with ammoniacal silver nitrate (fraction 3 and 4 gave practically no precipitates), gave red halochromism with sulfuric acid, and turned yellowish on a few hour's standing and also turned viscous on long standing. Analyses and molecular weight measurement of this fraction gave intermediate values between cyclohexanone and 3-cyclohexylidene-1-butyne.

Anal. Found: C, 81.07; H, 9.95; mol. wt., (Rast), 130. Calcd. for $C_6H_{10}O$ (cyclohexanone): C, 73.43; H, 10.27; mol. wt., 98.1. Calcd. for $C_{10}H_{14}$ (3-cyclohexylidene-1-butyne); C, 89.49; H, 10.51; mol. wt., 134.2. Calcd. for $C_{10}H_{16}O$ (III): C, 78.90; H, 10.60%; mol. wt., 152.2.

Fraction 2 had properties similar to those of fraction 1; the quantity obtained of cyclohexanone 2,4-dinitrophenylhydrazone was less than that from the latter, and, in addition, some amount of 2,4-dinitrophenylhydrazone of III was obtained.

Fraction 3 (III).—The fraction was redistilled, collecting ca. 3 g. of a fraction boiling at 105~110° (30 mm.). Most part of it consisted of 3-cyclohexylidene-2-butanone (III), which was ascertained from the quantity obtained of the 2,4-dinitrophenylhydrazone. It was only weakly positive toward Schiff reagent, readily decolorized bromine water, gave practically no precipitates with ammoniacal silver nitrate, and did not reduce Fehling solution. It gave a positive test for methyl ketone[8], fuchsine-red color being produced on heating with potassium hypobromite solution and pyridine. On refluxing the same fraction for ca. 1.5 hr. with a solution of phenylhydrazine hydrochloride in ethanolic acetic acid, colorless crystals were produced, which gave a pyrazoline reaction of wine-red coloration with sulfuric acid and sodium nitrite; the crystals were very easily soluble in aqueous methanol.

2,4-Dinitrophenylhydrazone of III was recrystallized from methanolic pyridine, deep yellow needles or crystals, easily soluble in pyridine, m. p. 123~124°.

Anal. Found: C, 57.53; H, 5.82; N, 16.83. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07; N, 16.86%.

Semicarbazone of III was recrystallized from methanol, colorless needles somewhat soluble in the same solvent, m. p. 174~175° (indefinite melting points reported[8] are: 180~184°, 155~160°, 160~163° in different preparations; the least soluble semicarbazone in the case of the fractional crystallization, m. p. 192~193° rapid heating), 187° (slow heating)).

6) Domenick Papa, Frank J. Villanits and Helen F. Ginsberg, *Arch. Biochem. Biophys.*, **33**, 482 (1951).
7) T. Takeshima, *J. Sci. Research Inst.*, **48**, 103 (1954).
8) J. Adachi, *Anal. Chem.*, **23**, 1491 (1951).

Anal. Found: N, 19.93. Calcd. for $C_{11}H_{19}ON_3$: N, 20.08%.

On adding 2,4-dinitrophenylhydrazine reagent directly to the semicarbazone, the corresponding 2,4-dinitrophenylhydrazone was obtained, which was identical with that of III mentioned above.

Hydrolysis of Fraction 3 (III).—A mixture of 0.5 g. of the above redistilled portion of fraction 3 and 3 cc. of ca. 80% formic acid and 0.5 cc. of 50% sulfuric acid, was boiled under reflux for ca. 3 hr. The reaction mixture was neutralized with a solution of potassium carbonate, extracted with ether, dried with potassium carbonate and distilled. A distillate up to ca. 40°, which consisted almost entirely of the solvent, was rejected. Next ethereal distillate, on treatment with 2,4-dinitrophenylhydrazine reagent, yielded yellow needles which melted at ca. 115°; the melting point was not depressed on admixture with an authentic sample of methyl ethyl ketone 2,4-dinitrophenylhydrazone. The higher boiling distillate, which amounted to a considerable quantity, was converted to cyclohexanone 2,4-dinitrophenylhydrazone which melted at 158~159°; the melting point was not depressed on admixture with the authentic sample.

Fraction 4, b. p. 132~138° (30 mm.), consisted almost only of 3-cyclohexyl-2-butenal (IV), which was ascertained from the quantity obtained of the 2,4-dinitrophenylhydrazone mentioned below. The fraction had a pleasant smell, gave positive test with Schiff reagent (violet color was gradually produced, which was accompanied with a formation of some dregs), reduced ammoniacal silver nitrate, decolorized bromine water, and gave a halochromic coloration with sulfuric acid; a trace of the aldehyde on contact with sulfuric acid turned into deep red and the whole became golden yellow when it was made uniform by shaking; the behavior was somewhat similar to that of III. It, on heating, merely turned Fehling solution into turbid bluish green and the oil became reddish, which seemed to be caused by fine particles of perhaps copper or cuprous oxide; the behavior resembled those of β-methylcrotonaldehyde and 3,4-dimethyl-2-hexenal[9].

It was slightly positive toward methyl ketone test[5], which may be due to contamination with III.

On heating with phenylhydrazine hydrochloride in ethanolic acetic acid, it gave an oily product which had a pyrazoline reaction of dark violet or bluish violet color quite different from that in the case of III.

2,4-Dinitrophenylhydrazone of IV. — The derivative of fraction 4 was recrystallized from pyridine. light red needles or long plates, m. p. 199~200°, easily soluble in hot pyridine and sparingly soluble in cold ethanol.

Anal. Found: C, 57.84; H, 5.91; N, 16.83. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07; N, 16.86%.

Semicarbazone of IV. — The semicarbazone of fraction 4 was recrystallized from methanol, colorless long plates or needles, m. p. 183~184° (slow heating), ca. 196° (rapid heating), easily soluble in hot ethanol.

Anal. Found: N, 20.05. Calcd. for $C_{11}H_{19}ON_3$: N, 20.08%.

The above 2,4-dinitrophenylhydrazone of IV was obtained also from this semicarbazone.

Dimedone Derivative of IV.—To a solution of ca. 0.1 g. of fraction 4 in ca. 4 cc. of 50% ethanol was added ca. 0.6 g. of dimedone and one drop of piperidine, and the mixture then was gently boiled for a while. After being cooled, a small quantity of water was added to the reaction mixture, and the resulting precipitates were collected, recrystallized from aqueous ethanol and then from methanol. Colorless crystals, m. p. 160~161°, fairly soluble in 50% ethanol.

Anal. Found: C, 75.11; H, 9.15. Calcd. for $C_{26}H_{38}O_4$: C, 75.32; H, 9.24%.

Ozonolysis of Fraction 4 (IV).—A solution of 0.5 g. of the fraction in ca. 16 g. of carbon tetrachloride was cooled with ice and ozonized oxygen was passed through for ca. 2 hr., and then the solvent was removed on a water-bath. The viscous product was shaken with aqueous methanol and the oily portion was treated with 2,4-dinitrophenylhydrazine reagent. The dark reddish brown viscous oil produced was recrystallized from methanolic pyridine to yield orange yellow fine needles, m. p. ca. 310°. Reported melting points of glyoxal 2,4-dinitrophenylosazone are: 311~312°[10], 326~328°[11], 318°[12].

Hydrogenation of Fraction 4 (IV). — The fraction was hydrogenated using palladium-kieselguhr catalyst. The greater part of the product distilled out at 112~115° (30 mm.), a colorless liquid which had a camphoraceous odor and produced deep pink color with Schiff reagent. It was considered to be 3-cyclohexylbutyraldehyde (V) and gave the derivatives mentioned below.

2,4-Dinitrophenylhydrazone of V. — It was recrystallized from methanolic pyridine to give deep yellow (tinged with orange) crystals, m. p. 125~127°; mixed melting point with 2,4-dinitrophenylhydrazone of III was 95~103°.

Anal. Found: C, 57.36; H, 6.46; N, 16.66. Calcd. for $C_{16}H_{22}O_4N_4$: C, 57.47; H, 6.63; N, 16.76%.

Semicarbazone of V. — It was recrystallized from methanol, colorless plates, m. p. 139~140°.

Anal. Found: C, 62.40; H, 9.69; N, 20.09. Calcd. for $C_{11}H_{21}ON_3$: C, 62.52; H, 10.02; N, 19.89%.

2,4-Dinitrophenylhydrazone of V was obtained also from the above semicarbazone.

Summary

The formic acid rearrangement of ethynylcarbinols has been extended to 2-cyclo-

9) T. Takeshima, *J. Sci. Research Inst.*, **45**, 103 (1951); *J. Am. Chem. Soc.*, **75**, 3309 (1953).

10) T. L. Jacobs and W. J. Whitcher, ibid., **64**, 2635 (1942).

11) H. H. Strain, ibid., **57**, 758 (1935).

12) C. Neuberg and E. Simon, *Biochem. Z.*, **256**, 488 (1932); J. Meisenheimer and W. Schmidt, *Ann.*, **475**, 181 (1929).

hexyl-3-butyn-2-ol(II), a model carbinol in which the tertiary carbon atom and the methyl group are adjacent to the carbon atom attached to the hydroxyl group. The major rearrangement product consisted of a mixture of 3-cyclohexylidene-2-butanone (III) (ca. 28% yield) and a new aldehyde, 3-cyclohexyl-2-butenal(IV) (ca. 12% yield). The latter was hydrogenated to give 3-cyclohexylbutyraldehyde (V). These compounds were isolated and characterized.

We wish to express our heartfelt thanks to Dr. T. Ukaji for his care kindly extended to us. Thanks are also due to Messrs M. Otsuka and N. Maejima for their kind assistance.

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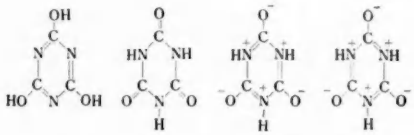
Magnetochemical Study of Cyanuric Acid, Melamine, and Some Derivatives

By Yoshio MATSUNAGA and Shiro MORITA*

(Received March 28, 1958)

The structure of highly symmetrical heterocyclic rings which appear in cyanuric acid and melamine has been the subject of much interest. Their structures in the solid state were established from X-ray studies. The former molecule[1] was found to be in the carbonyl form II and the latter[2] in the amide form V. Magnetic susceptibilities and anisotropies of cyanuric ring compounds have been examined by several investigators, but their conclusions as to the structure of cyanuric acid were conflicting. Pascal[3] concluded that the magnitude of the diamagnetic susceptibility favors form I, however, Maruha[4] suggested that its structure is a resonance hybrid of form II and the zwitter-ionic forms III and IV. On the other hand, Lonsdale[5] found that the cyanuric acid molecule has anisotropy of the same order as those of melamine and cyanuric triazide and she favored form I. Besides, the recorded values for cyanuric acid disagreed considerably as shown in Table I. Therefore, a more detailed examination of the diamagnetic susceptibilities of cyanuric acid and melamine, including also their derivatives which have no tautomeric forms, was undertaken.



(I) (II) (III) (IV)

Experimental

Materials.—Cyanuric chloride, commercial product, recrystallized from benzene, m.p. 146°C. Trimethyl cyanurate[6c], m.p. 135°C. Triphenyl cyanurate[6d], m.p. 230~231°C. Hexaethylmelamine[6b], b.p. 147~148°C/2.5 mmHg. Melamine, commercial product, recrystallized from water and sublimed in vacuo. Trimethylolmelamine, commercial product, dried in vacuo. 2,4-Dianilino-6-chloro-*s*-triazine[6a], sublimed in vacuo, m.p. 199°C. 2,4-Dianilino-6-methoxy-*s*-triazine[6c] sublimed in vacuo, m.p. 168°C. Melamine hydrochloride, prepared by dehydration in vacuo from hemihydrate. Cyanuric acid, supplied by Nippon Carbide Ind. Co., recrystallized from water repeatedly and sublimed in vacuo.

Magnetic measurements—The susceptibility measurements were carried out using a Gouy balance as previously described[7].

Results and Discussion

In Table I specific and molar susceptibilities together with other recorded values of the latter quantity are presented for

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1) E. H. Wiebenga, *J. Am. Chem. Soc.*, **74**, 6156 (1952).
2) E. W. Hughes, ibid., **63**, 1737 (1941).
3) P. Pascal, *Compt. rend.*, **176**, 1887 (1923).
4) J. Maruha, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **71**, 627 (1950).
5) K. Lonsdale, *Proc. Roy. Soc.*, **A177**, 272 (1941).
6) J. T. Thurston et al., *J. Am. Chem. Soc.*, **73**, 2981, 2984, 2986, 2990 (1951).
7) H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

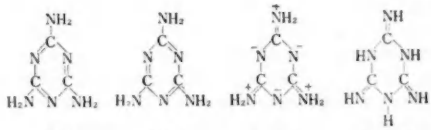
TABLE I

DIAMAGNETIC SUSCEPTIBILITIES OF CYANURIC ACID, MELAMINE, AND THEIR DERIVATIVES

	Substance	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ Obs.	Calc.	Lit.
I	Cyanuric chloride	0.435	80.2	82.1	81.1[10]
	Trimethyl cyanurate	0.525	89.9	89.9	—
	Triphenyl cyanurate	0.576	205.9	205.1	—
	Hexaethylmelamine	0.675	198.8	197.9	—
II	Melamine	0.502	63.3	60.8	65.2[11], 61.7[12]
	Trimethylolmelamine	0.519	112.2	110.2	—
	2,4-Dianilino-6-chloro-*s*-triazine	0.558	166.7	165.8	—
	2,4-Dianilino-6-methoxy-*s*-triazine	0.586	172.5	168.5	—
	Melamine hydrochloride	0.538	87.5	84.9	—
	Cyanuric acid	0.422	54.5	52.6	63.2[13], 50.5[14], 61.5[15]

ten compounds. The first group consists of four compounds which have no tautomeric form. On the basis of these experimental values we estimated the constant for unsubstituted triazine at -36.5[8] on the assumption that the magnetic contribution of substituents is just the same as in the case of derivatives of benzene. The molar susceptibilities in the fourth column were evaluated on the same assumption. Pascal[3] gave -36.5 for the contribution of the triazine ring and -1.85 for the correction term. Our values which must be compared with these two are -27.7 and $+6.95$. It must be noted that our values are in serious disagreement with Pascal's, but our correction term is close to those for the pyrimidine ring ($+6.5$) and for the pyrazine ring ($+9$) given by Pacault[9].

The agreement between the experimental and the calculated values in the case of the first group is satisfactory; however, it should be noted that in the second group the former values are appreciably and consistently more diamagnetic. The substances in the latter group have the amino nitrogen on which one or two hydrogen atoms remain, so they have the possibility of being in another form, the imide structure (for example, the form VIII of melamine). But from X-ray and spectroscopic studies[14,15], it seems to be unreasonable that the increase of diamagnetism is due to the structural change to the imide form.



(V) (VI) (VII) (VIII)

The contribution of the zwitter-ionic forms seems to be rather important in the melamine molecule. To explain the C-N bond lengths the three structures V, VI and VII must contribute nearly equally[2]. The conjugation between amino group and aromatic nucleus diminishes considerably in the derivatives of benzene, when the hydrogen atoms attached to the amino nitrogen are completely substituted by alkyl groups[16]. By analogy, it would seem that the increase of diamagnetism appearing in the substances in the second group relates to the extraordinarily large contribution of ionic structures.

We shall examine more quantitatively the magnitude of molar susceptibilities of these heterocyclic compounds. The value for the Kekulé-like form of unsubstituted triazine is estimated at -19.6 by Gray and Cruickshank's method[17]. If this value is equal to the isotropic contribution of the ring as is usual in aromatic nuclei, the molar anisotropy must be about -50. This is too large if we compare it with -30 reported by Lonsdale[18] for the molar anisotropy of

8) All values of susceptibility are in c. g. s. units and are multiplied by 10^6 throughout this paper.
9) A. Pacault, *Ann. chim.*, (12), **1**, 527 (1946).
10) J. Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).
11) I. E. Knaggs and K. Lonsdale, *Proc. Roy. Soc.*, **A177**, 140 (1940).
12) J. Ploquin and C. Vergneau-Souvray, *Compt. rend.*, **234**, 97 (1952).
13) S. K. Siddhanta and P. Ray, *J. Indian Chem. Soc.*, **20**, 359 (1943).
14) I. M. Klotz and T. Askounis, *J. Am. Chem. Soc.*, **69**, 801 (1947).
15) M. J. S. Dewar and L. Paoloni, *Trans. Faraday Soc.*, **53**, 261 (1957).
16) G. W. Wheland, "Resonance in Organic Chemistry", John Wiley & Sons, Inc., New York, (1955), p. 99-100.
17) F. W. Gray and J. H. Cruickshank, *Trans. Faraday Soc.*, **31**, 1491 (1935).
18) K. Lonsdale, *Z. Krist.*, **95**, 471 (1936).

cyanuric chloride. Such a discrepancy becomes more remarkable in the case of melamine. The calculated value for the form V or VI is -45.6 and the anisotropy given by the combination with the experimental molar susceptibility is equal to -53. On the other hand, Knaggs and Lonsdale's observed values are -58.1 for the isotropic contribution and -21 for the anisotropy. These disagreements suggest that the real isotropic contribution of a triazine ring is more diamagnetic than the calculated one and the resonance with the zwitter-ionic form brings about a marked increase of the isotropic diamagnetism.

As to cyanuric acid, the calculated value, obtained by assuming the presence of a triazine ring, is near the experimental one. However, this agreement cannot be considered as conclusive evidence for form I since we can say that the value of the molar susceptibility also favors the carbonyl form as discussed in the following paragraph.

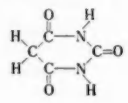
The structure of urea is closely similar to part of the carbonyl form of cyanuric acid. With this compound the resonance energy is relatively large. This fact suggests that resonance with the zwitter-ionic structures is important in this case too. The diamagnetism of urea was examined in detail by Clow[19]. The experimental values are in serious disagreement with the calculated ones for the carbamide structure especially in the case of urea itself and the monosubstituted derivatives. Therefore, it is no wonder that Gray and Cruickshank's method gives such unreasonable estimates as -39.3 for the isotropic contribution of the carbonyl form of cyanuric acid and -45.6 for the molar anisotropy.

Since Pascal determined his first constants, it has been well known that the magnetic contributions of oxygen and nitrogen atoms depend markedly on their surroundings. He gave many group constants in his second system of the additivity rule[20]. Some of them are cited in Table II. Using the constant for the amide group with substituent, we obtain -47.5 for the isotropic diamagnetism of the carbonyl form II and -21 for the molar anisotropy. The latter value is in good agreement with -24 given by Lonsdale[5]. The molecule of cyanuric acid contains a triazine ring only in the zwitter-ionic forms III and IV; hence the large anisotropy suggests that the contribution of these structures to a resonance hybrid is very important. This view is consistent with the evidence from other sources.

TABLE II
PASCAL'S CONSTANTS IN HIS SECOND SYSTEM

Group		Constant ($-\chi_M$)
C=O		8.1
C(=O)(-O)		15.15
C(=O)(-N)	(amide without substituent)	15.70
C(=O)(-N)	(amide with substituent)	13.83
O=C(-N)(-N)	(urea)	25.5

Recently Sato[21] measured the susceptibilities of barbituric acid (IX) and its many derivatives. Using the constants for the oxygen atoms in alcohol (-4.61) or the carboxyl group (-3.36) instead of that in ketone ($+1.72$), his calculated values were found to be in rather good agreement with the experimental ones. However, if we apply his procedure to cyanuric acid, the calculated values are -51.7 to -55.5 for the isotropic contribution of the carbonyl form and nearly zero to -8.4 for the molar anisotropy. This estimated anisotropy is in poor agreement with that reported by Lonsdale. The procedure which was applied successfully to the case of barbituric acid seems to be unreliable for cyanuric acid.


(IX)

Summary

The magnetic susceptibilities of melamine, cyanuric acid, and eight of their derivatives were measured by the Gouy method. On the basis of the molar susceptibilities of the four compounds which have no tautomeric form, the constant for triazine was estimated at -36.5. It appeared that Gray and

19) A. Clow, *Trans. Faraday Soc.*, **33**, 381 (1937); **34**, 457 (1938).
20) J. Hoarau, A. Pacault and P. Pascal, *Cahier de physique*, No. 74, p. 30 (1955).
21) Y. Sato, *Bull. Res. Inst. Non-Aqueous Solns. Tohoku Univ.*, **6**, 1 (1956).

Cruickshank's method gives too small an estimate for the isotropic part of the molar susceptibility in all cases and resonance with the zwitter-ionic structures brings about an increase of the isotropic diamagnetic contribution. With regard to cyanuric acid, the magnitude of the molar susceptibility seemed to be not inconsistent with the form containing a triazine ring. However, using Pascal's second additivity rule we found that both the magnitude of the isotropic diamagnetism and that of the molar anisotropy favor the carbonyl form.

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A Theoretical Consideration of Simple Catalytic Reactions. Decomposition of Gaseous Hydrides

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(Received February 11, 1958)

The thermal decomposition of gaseous hydrides on their own constituent elements to produce hydrogen gas is one of the simplest catalytic reactions. During the reaction, the surfaces of the elements are always renewed by the continuous deposition of fresh elements and only two elements are involved including the catalyst. The kinetics of such reactions are summarized in Table I. A similar reaction, the decomposition of nickel carbonyl, was also listed in the Table. The reason why the kinetics of these similar reactions are so different is to be treated here in a semi a priori fashion.

TABLE I

Kind of reaction	Kinetics of decomp.	Apparent activation energy
AsH_3 on As[1]	$v=kP_{AsH_3}$	23.2 kcal./mol·
SnH_4 on Sn[2]	$v=kP_{SnH_4}$	9.1
H_2Se on Se[3]	$v=kP_{H_2Se}$	
SbH_3 on Sb[4,5]	$v=kP_{SbH_3}^{0.6\sim1.0}$	8.8 at $P_{SbH_3}=40$cm.
CH_4 on C[6]	$v=\dfrac{kP_{CH_4}}{1+bP_{H_2}}$	53.4
$Ni(CO)_4$ on Ni[7,8]	$v=\dfrac{kP_{Ni(CO)_4}}{1+bP_{CO}}$	10.3, 12.0
GeH_4 on Ge[9]	$v=k$	41.2

As to the other gaseous hydrides, the decompositions of silane, SiH_4[10], and diborane, B_2H_6[11,12] have also been studied, but these decompositions were found to be homogeneous reactions. In the cases of methane[6,13,14], germane[9] and nickel carbonyl[9], both heterogeneous and homogeneous reaction take place under ordinary circumstances at their decomposition temperatures, but the heterogeneous reaction only is taken into account in Table I.

In the case of germane decomposition it has been shown in previous papers[9,15-17] that (1) the decomposition on germanium is a zero order reaction, and (2) during the decomposition the whole surface of the germanium is practically covered by chemisorbed hydrogen atoms the number of which is approximately equal to that of surface germanium atoms. (3) No hydrogen deuteride is formed by the decomposition of germane in the presence of an

1) K. Tamaru, *J. Phys. Chem.*, **59**, 777 (1955).
2) K. Tamaru, ibid., **60**, 610 (1956).
3) M. Bodenstein, *Z. physik. Chem.*, **29**, 429 (1899).
4) A. Stock et al., *Ber.*, **37**, 901 (1904); **40**, 532 (1907); **41**, 1309 (1908)
5) K. Tamaru, *J. Phys. Chem.*, **59**, 1084 (1955).
6) R. M. Barrer, *Proc. Roy. Soc.*, **A149**, 253 (1935).
7) A. P. Garratt and W. H. Thompson, *J. Chem. Soc.*, **1934**, 1882.
8) C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 440 (1935).
9) K. Tamaru, M. Boudart and H. Taylor, *J. Phys. Chem.*, **59**, 801 (1955).
10) T. R. Hogness et al., *J. Am. Chem. Soc.*, **58**, 108 (1936).
11) R. P. Clarke and R. N. Pease, ibid., **73**, 2132 (1951).
12) J. K. Bragg et al., ibid., **73**, 2134 (1951).
13) L. S. Kassel, ibid., **54**, 3949 (1932).
14) H. H. Storch, ibid., **54**, 4188 (1932).
15) P. J. Fensham, K. Tamaru, M. Boudart and H. Taylor, *J. Phys. Chem.*, **59**, 806 (1955).
16) K. Tamaru and M. Boudart, "Advances in Catalysis", Vol. IX, Academic Press Inc., N. Y. (1957), p. 699.
17) K. Tamaru, *J. Phys. Chem.*, **61**, 647 (1957).

excess of deuterium. (4) When the mixture of germanium hydride and deuteride are decomposed together, abundant quantities of equilibrated deuteride are produced. (5) No exchange takes place between the two kinds of germane. (6) The desorption rate of the chemisorbed hydrogen on germanium at full coverage is equal to the decomposition rate of germanium hydride. (7) The ratio of the decomposition rates of germane and deuterogermane is 1.8 to 1.

The zero-order kinetics and the observation 2 exclude the Eley-Rideal mechanism, i. e., involving collisions of germane molecules in the gas phase, or those in the van der Waals' adsorption layer with the chemisorbed species on the surface. The observations 2 and 3 exclude the possibility of hydrogen molecules splitting off from the germanium hydrides on the surface, such as, for example, $GeH_4(a) \rightarrow GeH_2(a) + H_2(g)$, throughout the decomposition, because this process will not give so much hydrogen deuteride as has been found in the product, bearing in mind that no exchange reaction between hydrogen and deutrium molecules takes place while germane is being decomposed.

The following mechanism for the decomposition is consistent with all the data;

$$GeH_4(g) \rightarrow GeH_3(a) + H(a) \quad (A)$$

$$GeH_3(a) \rightarrow GeH_2(a) + H(a) \quad (B)$$

$$GeH_2(a) \rightarrow GeH(a) + H(a) \quad (C)$$

$$2H(a) \text{ or } 2GeH(a) \rightarrow H_2(g) \quad (D)$$

and the last step, the desorption of hydrogen atoms to form hydrogen molecules, is a rate-determining step for the reaction. As the chemisorbed hydrogen covers the surface during the decomposition, the chemisorption of the germane, as will be shown later, is suppressed by the chemisorbed hydrogen and accordingly it appears most probable that as soon as the hydrogen desorbs, the step A takes place to keep the saturation of the surface, which results in the observation 5, no exchange between GeH_4 and GeD_4 being detected during the reaction.

For most of the other hydrides, the chemisorption step onto the surface could be considered as rate-determining from their kinetics. By making some assumptions we can expect to treat this kind of reaction with a statistical mechanical method to estimate the rate of each elementary step of the reaction and hence the order of reaction.

The rate of the heterogeneous elementary reaction V per unit surface area of catalyst surface is given by the following equation[18].

$$V = \frac{kT}{h} Gq^* \frac{N_a}{F_a^\circ} Q_{C^*(0)} \quad (1)$$

where G is the number of sites for the activated complex a^* per cm^2., q^* is the partition function of a^* and N_a is the concentration of initial reactant a in the gas phase, F_a° is the partition function of a per unit volume and $Q_{C^*(0)}$ is the probability that the sites for the activated complexes are vacant.

The following assumptions are used for the calculation of the rate of each elementary step of the decompositions.

(1) The bond energies between a hydrogenated element and the hydrogen atoms are the same for all the hydrogen atoms in the hydride molecule and are independent of the number of hydrogen atoms remaining within the hydride fragment.

(2) The translational, rotational and vibrational partition functions of the activated complexes of each elementary reaction and those of the chemisorbed radicals or molecules are taken as unity.

(3) All the elementary reactions other than the rate-determining step are rapid enough to be considered in equilibrium in the stationary state of the reaction.

(4) Each hydrogen atom of hydrides is assumed to split off one by one, as has been shown in the case of germane decomposition, and as each successive removal of a hydrogen atom accompanies an M–H bond cutting to form a M–M bond and an adjacent H(a), it is assumed that the true activation energy in each step is almost the same except the last step.

N_a in the Eqation 1 can be replaced by P_a/kT and T by $T_m e^{1-\frac{T_m}{T}}$, where T_m is the median of the reaction temperature range[18,19]. Thus

$$V = \frac{kT_m eG}{h} \frac{P_a}{F_a} Q_{C^*(0)} \exp\left(-\frac{\Delta^* E}{RT}\right) \quad (2)$$

where $F_a = \frac{kT_m}{B} F_a^\circ(T_m)\ e^{n+1}$ and n is the sum of the exponents of T in the translational and rotational partition functions, B, conversion factor from mmHg into

18) J. Horiuti, *Catalyst*, Inst. Catalyst Res., Hokkaido Univ., Sapporo, **2**, 1 (1947); **7**, 107 (1951).

19) T. Kwan, "Advances in Catalysis", Vol. VI Academic Press Inc., N. Y. (1954), p. 67.

c.g.s. unit, P_a, the pressure of a in mmHg, $F_a^\circ(T_m)$, translational, rotational and vibrasional partition functions of a at T_m, and Δ^*E is the difference of potential energy between the initial reactant a and the activated complex a^*. The values of F_a are listed in Table II.

TABLE II

T	a	F_a(mm.$^{-1}$)	a	F_a(mm.$^{-1}$)
551°K	AsH_3	3.2×10^{15}	H_2	4.2×10^{10}
350	SnH_4	1.1×10^{15}	H_2	8.6×10^{9}
573	H_2Se	2.8×10^{15}	H_2	4.8×10^{10}
308	SbH_3	0.9×10^{15}	H_2	5.5×10^{9}
1000	CH_4	5.0×10^{14}	H_2	3.4×10^{11}
381	$Ni(CO)_4$	6.5×10^{17}	CO	3.4×10^{13}
551	GeH_4	2.4×10^{15}	H_2	4.2×10^{10}

When a part of the catalyst surface is covered by the adsorption of a^*, etc., $Q_{C^*(0)}$ is expressed as follows;

$$Q_{C^*(0)}=\{Q_{C(a)}F_a\exp(-\Delta E(a)/RT)/P_a\}^\alpha \quad (3)$$

where $Q_{C(a)}$ is the probability that the sites for the adsorption are occupied by a, $\Delta E(a)$, the heat of adsorption of a, and α, the ratio of the number of lattice points for the activated complex over that for a, which is usually assumed to be unity.

Decomposition of Stibine on Antimony Surface.—The heat of the reaction is 34.8 kcal./mol.[20] and hydrogen does not chemisorb on an antimony surface[21]. The rate of each elementary reaction at 35° can be expressed as follows,

$$V_A=S(P_{SbH_3}/F_{SbH_3})Q_{C^*(0)}\exp(-\Delta^*E_A/RT)$$
$$=1.1\times10^{-15}SP_{SbH_3}\exp(-\Delta^*E_A/RT) \quad (4)$$

$$V_B=S(P_{SbH_3}/F_{SbH_3})(F_{H_2}/P_{H_2})^{\frac{1}{2}}\times\exp(-\Delta^*E_B/RT)Q_{C^*(0)}$$
$$=1.4\times10^{-2}S\frac{P_{SbH_3}}{\sqrt{P_{H_2}}}\times\frac{\exp(-\Delta^*E_A/RT)}{(1+1.4\times10^{-2}P_{SbH_3}/P_{H_2}^{\frac{1}{2}})} \quad (5)$$

$$V_C=\frac{2}{3}S\left(\frac{P_{SbH_3}}{F_{SbH_3}}\right)^{\frac{2}{3}}\exp(-\Delta^*E_C/RT)Q_{C^*(0)}$$
$$=0.6\times10^{-10}S(P_{SbH_3})^{\frac{2}{3}}\exp(-\Delta^*E_C/RT) \quad (6)$$

where V_A, V_B and V_C are the rates of the following elementary reactions, respectively,

$$SbH_3(g)\rightarrow SbH_2(a)+H(a) \quad (A)$$
$$SbH_2(a)\rightarrow SbH(a)+H(a) \quad (B)$$
$$2SbH(a)\text{ or }2H(a)\rightarrow H_2(g) \quad (C)$$

and S is $kTGe/h$ and Δ^*E_A, Δ^*E_B and Δ^*E_C are the activation energies for the steps, A, B and C, respectively.

The temperature, T_c, at which V_A and V_C are equal can be obtained by putting $V_A=V_C$.

$$T_c=\frac{\Delta^*E_C-\Delta^*E_A}{2.30R[(1/3)\log(F_{SbH_3}/P_{SbH_3})+\log(2/3)]}$$
$$=(\Delta^*E_C-\Delta^*E_A)/(21.6-1.52\log P_{SbH_3}) \quad (7)$$

Above this temperature V_A controls the overall rate and below this temperature V_C controls the rate, provided Δ^*E_C is larger than Δ^*E_A. In other words, at higher temperatures the decomposition is of first order, while at lower temperatures it is proportional to 2/3 power of the stibine pressure, being independent of hydrogen pressure. In the transition region of the two, at higher stibine pressures the activation energy becomes larger, as V_C controls the rate more predominantly, and at lower pressures vise versa from the Equation 7.

As shown in a previous paper[5] the observed activation energy for this reaction is dependent upon the partial pressure of stibine and decreases as the pressure decreases, and the order of the reaction increases as the reaction temperature becomes higher from a fractional order to a first order. Hence the experimental results seem to support those theoretical conclusions, if it is tentatively assumed that the difference between Δ^*E_C and Δ^*E_A is around 6 kcal./mol. provided that all the other assumptions are valid.

Another explanation of the experimental results is the interpretation of the fractional order on the basis of the Langmuir concept, assuming that the adsorption of SbH_3(a) is appreciable. As has been discussed in the previous paper[5], however, this explanation seems to have little physical meaning according to Boudart[22].

Decomposition of Arsine on an Arsenic Surface at 278C°.—The heat of the reaction at 551°K is 38.6 kcal./mol. from the value at standard temperature and the

20) "Handbook of Chemistry and Physics", 35th Edition, by C. D. Hodgman et al., Chemical Rubber Publishing Co., Ohio. (1953).
21) B. M. W. Trapnell, "Advances in Catalysis," Vol. IX., Academic Press Inc., N. Y., (1957), p. 238.
22) M. Boudart, "Structure and Properties of Solid Surfaces", edited by G. R. Gomer and C. S. Smith, University of Chicago Press Chicago, Illinois, (1953) p. 400.

heat capacities of the gases[23], the followings are the results of a similar calculation for the decomposition.

$$V_A = 3.1\times10^{-16} S P \exp(-\Delta^*E_A/RT) \quad (8)$$

$$V_B = 8.3\times10^{-6} S(P_{AsH_3}/P_{H_2}^{\frac{1}{2}}) \times\exp(-\Delta^*E_A/RT) \quad (9)$$

$$V_C = 3.1\times10^{-11} S P_{AsH_3}^{\frac{2}{3}} \exp(-\Delta^*E_C/RT) \quad (10)$$

where Δ^*E_C in the Equation 10 is the true activation energy for the step C. The overall reaction is first order as is shown by the experiments, step A being rate-determining, provided that $\Delta^*E_C - \Delta^*E_A <$ 10 kcal. If this is the case and all the other assumptions are valid, T_c, where V_A equals to V_C, becomes lower than 200°C at 100 mm. of arsine pressure from the similar calculations and above this temperature the decomposition will be first order, which is the case in the experiments.

Decomposition of Methane on Carbon Surface.—The decomposition of methane on a carbon surface at 1000°K can be treated in the same way. The change of the heat content in this decomposition, ΔH, is 21.6 kcal. per mole at this temperature, as ΔH at 25°C is 17.89 kcal./mol.[22] and $\Delta C_p = 9.18 - 5.96\times10^{-3}T - 0.051\times10^5 T^{-2}$[24].

According to Barrer[6], the heat of adsorption of hydrogen on carbon is about 50 kcal./mol. being independent of its coverage. The results of the calculation are as follows, if we use the same suffixes for V_A, V_B, V_C and V_D as in the germane decomposition.

$$V_A = S(P_{CH_4}/F_{CH_4})\exp(-\Delta^*E_A/RT)Q_{C^*(0)} = 2.0\times10^{-15} S \frac{P_{CH_4}\exp(-\Delta^*E_A/RT)}{1+0.24\,P_{H_2}} \quad (11)$$

if it is noted that the step A takes place on the unsaturated carbon bonds on the surface and hence

$$Q_{C^*(0)} = \frac{1}{1+(P_{H_2}/F_{H_2})\exp(50{,}000/RT)}$$

and

$$V_B = S\frac{P_{CH_4}}{F_{CH_4}}\left(\frac{F_{H_2}}{P_{H_2}}\right)^{\frac{1}{2}} Q_{C^*(0)}\exp(-\Delta^*E_B/RT) = 2.1\times10^{-9} S \frac{P_{CH_4}}{P_{H_2}^{\frac{1}{2}}}\frac{\exp(-\Delta^*E_A/RT)}{1+0.23\,P_{H_2}} \quad (12)$$

$$V_C = S\frac{P_{CH_4}}{F_{CH_4}}\frac{F_{H_2}}{P_{H_2}} Q_{C^*(0)}\exp(-\Delta^*E_C/RT) = 2.1\times10^{-2} S \frac{P_{CH_4}}{P_{H_2}}\frac{\exp(-\Delta^*E_A/RT)}{1+0.23\,P_{H_2}} \quad (13)$$

as Δ^*E_B and Δ^*E_C are equal to $\Delta^*E_A - \frac{1}{3}(25{,}000-21{,}600)$ and $\Delta^*E_A - \frac{2}{3}(25{,}000-21{,}600)$, respectively and the coverage of CH(a), $Q_{C^*(CH(a))}$, of $H_2(g) \rightleftarrows 2H(a)$, are appreciable according to the calculation. On the other hand,

$$V_D = 8.0\,S\frac{P_{CH_4}^{\frac{1}{2}}\exp(-\Delta^*E_{0D}/RT)}{(1+4.0\,P_{CH_4}^{\frac{1}{2}})^2} \fallingdotseq \frac{S}{2}\exp(-\Delta^*E_{0D}/RT) \quad (14)$$

which is obtained from the following equations,

$$V_D = \frac{S}{2}\left(\frac{P_{CH_4}}{F_{CH_4}}\right)^{\frac{1}{2}} Q_{C^*(0)}\exp(-\Delta^*E_D/RT)$$

$$\theta_H/(1-\theta_H) = (P_{CH_4}/F_{CH_4})^{\frac{1}{2}} \times\exp\left(\frac{-25{,}000\times4+21{,}600}{4RT}\right) = 4.0\times P_{CH_4}^{\frac{1}{2}}$$

$$Q_{C^*(0)} = (1-\theta_H)^2$$

$$\Delta^*E_D = \Delta^*E_{0D} - \frac{1}{2}(25{,}000\times4-21{,}600)$$

where $\Delta^*{}_0E_D$ is the true activation energy for the step D.

The observed activation energy for this reaction is 53.4 kcal. and $\exp(70{,}000/RT)$ is equal to 2.0×10^{15}. Hence the step A is rate-determining, if Δ^*E_{0D} is less than 120 kcal./mol., which is most probably the case.

Barrer found that a kinetic expression,

$$V = \frac{kP_{CH_4}}{1+0.022\,P_{H_2}}$$

is applicable to this reaction, which is in fair agreement with the theoretical equation 11, if the ambiguity of the heat of adsorption of hydrogen on carbon is taken into account. As $\exp(30{,}000/RT)$ is equal to 3.6×10^6, the assumption 4 of the equal activation energies can be adjusted to nearly 30 kcal. for the step B, if all the other assumptions are valid.

Decomposition of Germane on a Germanium Surface at 302°C.—The results of a similar calculation are as follows, as the heat of adsorption of hydrogen on

23) F. D. Rossini and D. D. Wagman, "The Selected Values of Chemical Thermodynamic Properties," U. S. Government Printing Office (1952).
24) Kelley, Bull. of Bur. of Mines, No. 407 (1937).

germanium is 23.5 kcal./mol. at low coverages[17].

$$V_A = S\frac{P_{GeH_4}}{2.4\times10^{15}}\left(\frac{1}{1+0.23\sqrt{P_{H_2}}}\right)^2 \times\exp\left(-\Delta^*E_A/RT\right) \quad (15)$$

$$V_B = S\frac{P_{GeH_4}}{F_{GeH_4}}\left(\frac{F_{H_2}}{P_{H_2}}\right)^{\frac{1}{2}}\times\exp\left[-\left(\Delta^*E_A - \frac{1}{3}(q+11{,}800)\right)\Big/RT\right]Q_{C^*(0)}$$

$$= \frac{3.1\times10^{-10}SP_{GeH_4}\exp\left[-(\Delta^*E_A - q/3)/RT\right]}{(1+0.23P_{H_2}^{\frac{1}{2}})^2 P_{H_2}^{\frac{1}{2}}} \quad (16)$$

$$V_C = \frac{2.3\times10^{-2}SP_{GeH_4}\exp\left[-(\Delta^*E_A - 2q/3)/RT\right]}{P\left[1+0.23P_{H_2}^{\frac{1}{2}}+0.023\frac{P_{GeH_4}}{P_{H_2}}\exp\left(\frac{2q}{3RT}\right)\right]^2} \quad (17)$$

$$V_D = \frac{S}{2}\exp\left(-\Delta^*E_{0D}/RT\right) \quad (18)$$

where q is the heat of the reaction and Δ^*E_{0D} is the true activation energy for the step D. As the decomposition is probably exothermic, either V_A or V_D is the rate-determining step.

The experimental results show that the step D is the rate-determining step and the observed activation energy is 41.2kcal./mol. As $\exp(41{,}200/RT)$ is equal to 2.2×10^{15} at 302°C, V_D can be slower than V_A by 10^2 at the slowest at 10 cm. pressure of germane if Δ^*E_A is small enough. As will be shown later the observed reaction rate agrees satisfactorily with the calculated V_D. In the cases of the decompositions of tin hydride, arsine, etc., on the other hand, in which the step A is rate-determining, the partition functions of the activated complexes of V_A are usually not unity, but have fairly large values, which is probably the case in V_A of the Equation 15. This is probably one of the reasons why the step D is rate-determining, and, consequently, at much higher temperatures it can be expected that the reaction becomes first order in respect to germane, V_A being rate-determining, as the apparent activation enenrgy of V_A is smaller than Δ^*E_{0D}.

The fact that no exchange between GeD_4 and GeH_4 to form GeH_xD_y is observed during the reaction is explained by the slow rate of chemisorption of germane on the germanium surface, as the rate of chemisorption is retarded by the chemisorbed hydrogen atoms which cover the surface. If the desorption of hydrogen is assumed to be the only rate-determining step, the adsorption rate of germane onto the surface is so retarded by the chemisorbed hydrogen that it turns out slower than the desorption rate from the calculation. This implies that the adsorption rate is so retarded by the chemisorbed hydrogen atoms that another potential energy cascade appears at this adsorption step besides the desorption step, while the germanium surface is still almost saturated in this case.

Decomposition of Other Hydrides and Nickel Carbonyl.—The decomposition of tin hydride on tin surfaces can be treated in the similar way. It can be shown that the step A is rate-determining and the reaction is first order as in Table I, provided that the heat of the reaction is between 40 and −40 kcal./mol. and Δ^*E_{0D} is not larger than 20 kcal./mol.

In the case of the decomposition of hydrogen selenide, a similar calculation shows that it should be of first order in respect to hydrogen selenide.

The decomposition of nickel carbonyl on nickel surface can be treated in a similar way, though the nature of the chemical bonds between CO and nickel atom are different from those in the hydrides. The heat of the decomposition was given by Fischer et al.[25] The results of the calculation showed that the chemisorption of nickel carbonyl on nickel surface is rate-determining, having the kinetic expression of $v = kP_{Ni(CO)_4}/(1+bP_{CO})$ as Bawn has observed. The value of b in the expression was also computed with a reasonable agreement.

The observed and the calculated reaction rates are shown in Table III, where the unit of pressure, P, is mmHg. and the activation energy at 10 cm. stibine pressure is used for stibine decomposition; the tin and germanium surface are considered to be smooth. In these calculations the number of the sites for the reactions per cm.^{2}, G, is taken as 10^{15}. The discrepancies between the observed and

TABLE III

	Temp.	Observed rate	Calculated rate
GeH_4	302°C	5.2×10^{13}	0.5×10^{13} mol./sec. cm.^{2}
AsH_3	278	7.9×10^{9} P	6.0×10^{9} P
SbH_3	35	8.2×10^{10} P	3.6×10^{9} P
SnH_4	77	2.3×10^{13} P	3.7×10^{7} P

25) A.K. Fischer et al., *J. Am. Chem. Soc.*, **79**, 2044 (1957).

the calculated values are probably due to the large values of the partition functions of the activated complexes, not being unity.

The number of collisions of gas molecules on unit surface area per second (n_c) and that of reacted molecules (n_r) are shown in Table IV, where Δ^*E is the observed activation energy for the reaction. In the case of germane decomposition it is shown that $n_c \exp(-\Delta^*E/RT)$ is much smaller than n_r, which suggests that the rate-determining step is not the chemisorption step on bare surface.

TABLE IV

	Temp.	n_c	$n_c \exp\left(\frac{-\Delta^*E}{RT}\right)$	n_r
GeH_4	302°C	1.7×10^{20} P	3.7×10^{4} P	5.2×10^{13}
AsH_3	278	1.7×10^{20} P	1.1×10^{11} P	0.8×10^{10} P
SbH_3	35	1.8×10^{20} P	3.3×10^{15} P	0.8×10^{11} P
SnH_4	77	1.7×10^{20} P	3.5×10^{14} P	2.3×10^{13} P

A tin surface, for instance, does not chemisorb hydrogen[26], nevertheless it chemisorbs tin hydride to decompose it to tin and hydrogen. This chemisorption depends upon the bond strength between the chemisorbed species and the element, and if the total strength of the dissociative adsorption is strong enough to chemisorb, the chemisorption takes place to decompose the hydride. Thus hydrogen from hydride might be chemisorbed on the elements on which hydrogen gas is not chemisorbed. The fact that arsine can be decomposed on antimony more rapidly than on an arsenic surface[1], or that ammonia can be decomposed on germanium[27] might be explained on this basis.

Summary

The decomposition of arsine, stibine, tin hydride, methane, germane, hydrogen selenide and nickel carbonyl on the surface of the corresponding elements have been discussed from the statistical mechanical view-point. As these decompositions are catalytic reactions of the simplest type, several reasonable assumptions enable us to calculate the rates of each elementary step of each reaction and hence to decide the rate-determining step in a semi a priori fashion. It is shown that the calculations impose definite limitations to the possible mode of decompositions of this kind.

The author wishes to express his thanks to Dean Hugh Taylor and Professor W. J. Kauzmann of Princeton University and also to Professor J. Horiuti, Professor T. Kwan and Professor K. Miyahara of Hokkaido University for their valuable suggestions and encouragement.

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26) B. M. W. Trapnell, *Proc. Roy. Soc.*, **A218**, 566 (1953).

27) K. Tamaru, *J. Phys. Chem.*, **60**, 612 (1956).

Studies of Aggregation of Dodecylammonium Carboxylates in Carbon Tetrachloride by Infrared Absorption Spectra and Thermistors

By Ayao KITAHARA

(Received March 15, 1958)

It was reported that the phenomenon of solubilization by some detergents takes place in carbon tetrachloride solutions as happens in other non-polar solvents[1], though Palit et al.[2] had reported the occurrence of erratic behavior in carbon tetrachloride. Hence, it is considered necessary to investigate micelle formation or aggregation in carbon tetrachloride solutions of detergents by some direct method.

For the present purpose, studies by infrared spectroscopy and on the vapor pressure depression by the use of a couple of thermistors were carried out at varying concentrations. Results obtained by both of these independent methods were compared.

Experimental

Materials. — Dodecylammonium butyrate and dodecylammonium caprylate, the preparation of which had been described previously[1], were employed as detergents. Carbon tetrachloride was distilled after drying over calcium chloride or phosphorus pentoxide and the constant boiling center cut used.

Measurements. — Infrared spectra were obtained using a Perkin-Elmer 21 instrument with rock salt optics. Cells of 1 and 0.5 mm. thickness were used. Room temperature was controlled to about 20°C. Measurements of vapor pressure depressions using a couple of matched thermistors made it possible to calculate the apparent mean aggregation number (Z) which is evaluated involving the monomer present. The apparatus and the method were the same as those described in the previous paper[3]. The temperature of thermostat was controlled to 19.7 ± 0.0005°C. The calibration curve of the thermistor resistance vs. concentration was made using carbon tetrabromide as solute, because it will be safely said that solutions of carbon tetrabromide in carbon tetrachloride are ideal. Measurements by thermistors were made in triplicate or quadruplicate at each concentration and the average value was adopted for the calculation of Z.

1) A. Kitahara, *J. Colloid Sci.*, **12**, 342 (1957).
2) S. R. Palit and V. Venkateswarlu, *Proc. Roy. Soc.*, **A208**, 542 (1951).
3) A. Kitahara, This Bulletin, **31**, 288 (1958).

Results and Discussion

Assignment of Infrared Spectra.—The infrared spectra of detergents in carbon tetrachloride were depicted in Fig. 1 ranging from 1600 to 1750 cm^{-1} at varying concentrations. Absorption bands which become remarkable with increasing concentration are found at 1640 cm^{-1} in both spectra of dodecylammonium butyrate and

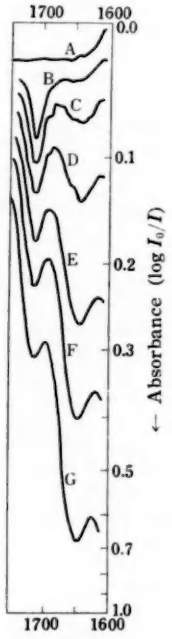


Fig. 1 (a). Change in infrared spectra of dodecylammonium butyrate with varying concentration. (A) pure solvent; (B) 0.0025mole/l.; (C) 0.0050 mole/l.; (D) 0.010 mole/l.; (E) 0.020 mole/l.; (F) 0.030 mole/l.; (G) 0.050 mole/l. Cell length: 1 mm.

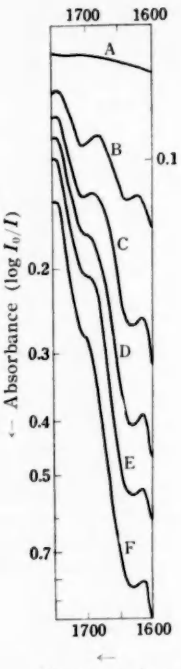
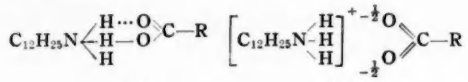


Fig. 1 (b). Change in infrared spectra of dodecylammonium caprylate with varying concentration. (A) pure solvent; (B) 0.018 mole/l.; (C) 0.036 mole/l.; (D) 0.055 mole/l.; (E) 0.073 mole/l.; (F) 0.112 mole/l. Cell length: 0.5 mm.

caprylate. On the other hand, it is seen that the absorption bands of 1710 cm^{-1} in neither of these spectra are sensitively variable with increasing concentration. Yeager and Barrow[4] have shown from infrared spectra of the reaction products of acetic acid and *n*-butylamine, diethylamine or triethylamine that the absorption bands of 1712 and 1630 cm^{-1} are assigned to the carbonyl group forming a hydrogen bonds with the same or another molecule and to the NH_2^+ or NH_3^+ group of the ammonium salt, respectively. The absorption band of "Amino-Acid I" which falls within the narrow range of 1640~1610 cm^{-1} for many monoamino-monocarboxylic acids has been assigned to NH_3^+ by many authors[5]. Hence, it may be concluded that the absorption bands of 1710 and 1640 cm^{-1} belong to the molecules of following formulae A and A_1, respectively:



(A) (A_1)

It will be thought that the molecule of A_1 aggregates to λ-mer in a non-polar solvent by virtue of ionic parts. Then the following equilibrium will exist in the carbon tetrachloride solutions:

$$A \rightleftarrows A_1 \rightleftarrows 1/\lambda A_\lambda \qquad (1)$$

where A_λ represents a λ-mer molecule. It is safely assumed that aggregation does not affect the absorption band, because aggregation will not be so strong as to affect chemical bonding, and that the greater part of molecules of A_1 exists in the aggregated state instead of the monomeric form because of the highly polar part. Hence, the equilibrium 1 can be rewritten as follows:

$$\lambda A \rightleftarrows A_\lambda \qquad (2)$$

The absorption bands of 1710 and 1640 cm^{-1} are characteristic for the molecule existing as monomer and the one taking part in aggregation, respectively. This assignment is consistent with the fact that the infrared spectra of these detergents by the potassium chloride disc method which represent the absorption band in the solid state show the more intense absorption at the 1640 cm^{-1} than those of the relatively concentrated solutions and show no absorption at the 1710 cm^{-1}. The absorbances ($\log I_0/I$) of each absorption band, which are shown in Table I, were obtained using the base-line method and the peak-intensity method from Fig. 1.

Analysis of Absorbance Data.—Aggregation equilibrium of a detergent in a non-polar solvent can be described by the Equation 2. The true aggregation number λ is evaluated by excluding the monomer present in the solution. It may be assumed that the aggregates are approximately monodisperse in a non-polar solution of the detergents[3]. No shift in the absorption band of 1640 cm^{-1} which is characteristic for the aggregate is evident from Fig. 1. This fact may be considered as an evidence of forming a single kind of aggregation[6]. The equilibrium constant is represented using molar concentration instead of activity, which is valid

4) E. A. Yeager and G. M. Barrow, *J. Am. Chem. Soc.*, **76**, 5211 (1954); **77**, 4474, 6206 (1955).
5) L. T. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Co., London, (1954), p. 204.
6) N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951).

TABLE I

THE VALUES OF ABSORBANCE (cell thickness: 1 mm.)

Dodecylammonium Butyrate					Dodecylammonium Caprylate				
Concentration (mole/l.)	Absorbance				Concentration (mole/l.)	Absorbance			
	D_a		D_1			D_a		D_1	
	B. L.*	P. I.*	B. L.	P. I.		B. L.	P. I.	B. L.	P. I.
0.0025	0.010	0.018	0.047	0.060	0.018	0.034	0.20_8	0.050	0.13_7
0.0050	0.016	0.050	0.053	0.082	0.036	0.080	0.47_2	0.050	0.23
0.010	0.035	0.11_5	0.055	0.11	0.055	0.18	0.76_4	0.060	0.29
0.020	0.070	0.24_5	0.065	0.15_5	0.073	0.24	1.02	0.060	0.36_4
0.030	0.12	0.38	0.075	0.21	0.112	0.42	1.62	0.070	0.50_4
0.050	0.23	0.65_7	0.085	0.28_5					

* B. L. ...Base line method, P. I. ...Peak intensity method

for the dilute concentration range under consideration. That is,

$$C_\lambda / C_1^\lambda = K \tag{3}$$

where C_λ and C_1 are the molar concentration of λ-mer and monomer, respectively. Beer's law of absorption is approximately obeyed for absorption bands of the monomer and of the detergent molecule taking part in aggregation in these dilute concentration ranges. Hence,

$$\left.\begin{aligned}(\log I_0/I)_1 &= k_1 C_1 l = D_1 \\ (\log I_0/I)_a &= k_a C_a l = D_a\end{aligned}\right\} \tag{4}$$

where k, C and l are the extinction coefficient, the molar concentration in monomer unit and a length of the cell, respectively. The subscripts of 1 and a represent a coexisting monomer and a detergent molecule taking part in aggregation, respectively. By definition,

$$C_a = \lambda C_\lambda \tag{5}$$

The following equation is deduced from the Equations 3, 4 and 5:

$$\lambda \log D_1 - \log D_a + k' = 0 \tag{6}$$

where $k' = \log\{\lambda k_a l K / (k_1 l)^\lambda\}$

As it has been assumed that λ is constant, k' is constant. The values of λ and k' can be calculated by means of the Equation 6 using the data of Table I. The values of λ calculated by means of the least square are given in the 2nd and 3rd columns of Table II.

TABLE II

THE VALUES OF TRUE AGGREGATION NUMBER (λ)

	Spectral method		Thermistor method
	Base line	Peak intensity	
Dodecylammonium butyrate	2.7	2.4	2.8
Dodecylammonium caprylate	3.3	2	3.0

In order to ascertain the result obtained above, the absolute intensity method was employed for comparison. Integrated densities (D_A) of absorption bands were calculated from the values of measurements for both bands of 1640 and 1710 cm^{-1} at a few concentrations of these detergents in carbon tetrachloride. These measurements* were carried out by means of a Perkin-Elmer 112 instrument with calcium fluoride prism. Room temperature was 25±1°C. Integrated density is represented by the following form[7]:

$$D_A = K \ln (I_0/I)_{\nu_{max}} \Delta\nu_{1/2}$$

where $\ln (I_0/I)_{\nu_{max}}$ is the apparent peak intensity, $\Delta\nu_{1/2}$ the apparent half-intensity band width and K the constant which is determined by $\ln (I_0/I)_{\nu_{max}}$ and $S/\Delta\nu_{1/2}$ (S is the slit width). The λ's were calculated from the Equation 6 using the values of D_A instead of the absorbances in Table I. The λ's obtained thus were approximately equal to 2 for both detergents. The agreement between those values and those from the peak intensity in Table II is satisfactory. The difference between the values from the absolute intensity and those from the base line is not serious, since it is sufficient only if we confirm the agreement of the order of magnitude of aggregation.

Analysis of Data by Thermistor.—The apparent mean aggregation numbers Z obtained by the thermistor method are shown in Table III. The fraction of the solute

* These measurements were carried out in cooperation with Mr. Suetaka by suggestion of Professor K. Kojima of Tokyo Institute of Technology, to whom the author wishes to express his sincere gratitude.

7) D. A. Ramsey, ibid., **74**, 72 (1952); J. Wenograd and R. T. Spurr, ibid., **79**, 5844 (1957).

TABLE III
THE VALUES OF Z, α, C_1 AND λ

	Concentration (C) (mole/l.)	Z	α	C_1 (mole/l.)	λ
Dodecylammonium butyrate	0.085_5	1.8	0.32	0.026	2.8
	0.050	1.5_5	0.43_5	0.022	2.6
	0.035	1.6	0.47_5	0.016_5	3.6
	0.017	1.2	0.71	0.012	2.1
	0.009	≈1.0	≈1.0	—	—
Dodecylammonium caprylate	0.111	2.0	0.24	0.027	3.0
	0.073	1.7_5	0.31	0.023	2.7
	0.055	1.7_5	0.35_5	0.020	3.0
	0.036_5	1.6_5	0.43	0.016	3.2
	0.018	≈1.0	≈1.0	—	—

present as the monomer (α) which is equal to C_1/C can be calculated by means of the following Kreuzer's equation[8]:

$$\ln(1/\alpha) = (Z-1)/Z + \int_0^C \{(Z-1)/ZC\}dC \quad (7)$$

where C is the total concentration of the solute. The values of C_1 are, therefore, calculated at each total concentration. The values of α and C_1 are given in the 4th and 5th columns of Table III. The following relations are deduced for the equilibrium 2 under an assumption that λ and K are constant[8,9]:

$$C - \lambda C/Z = -(\lambda-1)C_1$$

or
$$\lambda = (1-\alpha)/(1/Z-\alpha). \quad (8)$$

The values of the true aggregation number λ calculated using the Equation 8 are given in the last colum of Table III. The mean values of λ are given in the 4th column of Table II.

It is evident from Table II that the agreement between the values of λ obtained by both spectral and thermistor methods is satisfactory as for the order of magnitude of aggregation. This gives us an evidence to an assumption made in the derivation of the Equation 8. The true aggregation numbers λ of these detergents in carbon tetrachloride solutions are relatively smaller than those in cyclohexane solutions[3]. This fact corresponds qualitatively to the solubilizing power in carbon tetrachloride which is smaller than that in cyclohexane[1].

The Critical Micelle Concentration.— These aggregates may be regarded as small micelles. It has been shown experimentally[10] and theoretically[11] that formation of small micelles gradually takes place over an extended range of concentration. Hence, the critical micelle concentration (cmc) may not be sharply determined. The values of the cmc were tentatively evaluated by plotting C_1 in Table III vs. C and extrapolating to $C_1=C$. These cmc's are 0.010±0.001 and 0.013±0.001 mole/l. for dodecylammonium butyrate and caprylate, respectively. The plot of absorbance (D_1 and D_a) from base line method vs. total concentration (C) was depicted in Fig. 2.

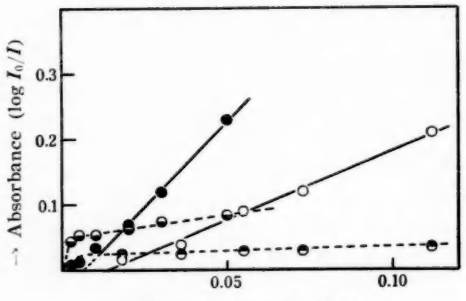


Fig. 2. Plots of absorbance (log I_0/I) versus concentration.
○ Plot for absorption at 1640 cm^{-1} of dodecylammonium caprylate
◓ Plot for absorption at 1710 cm^{-1} of dodecylammonium caprylate
Cell length, 0.5 mm.
● Plot for absorption at 1640 cm^{-1} of dodecylammonium butyrate
◒ Plot for absorption at 1710 cm^{-1} of dodecylammonium butyrate
Cell length, 1 mm.

It is evident from Fig. 2 that the relation between D_a and C is approximately linear excepting the range of lower concentra-

8) J. Kreuzer, *Z. physik. Chem.*, **B53**, 213 (1943).
9) I. Prigogine and R. Defay, "Chemical Thermodynamics", Longmans Green and Co., London, (1954), p. 422.
10) E. F. Williams, N. T. Woodberry and J. K. Dixon, *J. Colloid Sci.*, **12**, 452 (1957).
11) J. Stauff, *Z. Elektrochemie*, **59**, 246 (1995).

tions in the case of dodecylammonium butyrate where the experimental error is appreciable. It will be reasonable to assume that extrapolation of the $D_a \sim C$ line to zero concentration shows the cmc. These cmc's are 0.007 ± 0.001 and 0.013 ± 0.002 mole/l. for dodecylammonium butyrate and caprylate, respectively. The values obtained using the peak intensity by a similar way were 0.002 ± 0.001 and 0.006 ± 0.002mole/l., respectively. The agreement between the cmc's obtained by spectral and thermistor method is satisfactory as for the order of magnitude. On the other hand, these cmc's do not show good concordance with values obtained by solubilization of water which were 0.016 ± 0.002 and 0.035 ± 0.005 mole/l.*, respectively. This may be considered to indicate that the cmc has an extended range of concentration or that the cmc may be affected by the presence of water.

Solubilization which takes place in these solutions may be a type similar to that by adsorption on polar groups of small micelles by McBain et al.[12], though polar groups will be properly present in the interior of the aggregate in these non-polar solutions.

Summary

Measurements of infrared absorption spectra and of vapor pressure depressions using a couple of matched thermistors were carried out with carbon tetrachloride solutions of dodecylammonium carboxylates at varying concentrations. The absorption bands at 1710 and 1640 cm^{-1} were assigned to the carbonyl group of the monomer molecule which is formed by hydrogen bonding between amine and acid, and to the NH_3^+ group of ammonium salt resulting from the aggregation, respectively. The equation which was derived from the Beer's law and the aggregation equilibrium made it possible to calculate the true aggregation number λ using the values of absorbance at each absorption band.

Alternatively, the λ was calculated by means of the Kreuzer's equation from the apparent mean aggregation number Z which was obtained using thermistors. The agreement between the λ's obtained by the spectral and thermistor methods was satisfactory as for the order of magnitude. The cmc was tentatively estimated by both spectral and thermistor method.

The agreement between the cmc's obtained by these independent methods was good. But these cmc's did not show good agreement with those obtained from solubilization.

The author wishes to express his thanks to Dr. Yukio Mikawa for the measurement of infrared spectra, to Dr. Hiroshi Tubomura for his suggestions with the infrared analysis and to Professor Hideo Akamatu for his continuing interest in this study.

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* These values are those at 18 ± 2°C instead of those at 26°C in Ref. 1.

12) J. W. McBain and H. McHan, *J. Am. Chem. Soc.*, **70**, 3838 (1948).

Aconite Alkaloids.—On Pyrolytic Products of Aconitine, Oxonitine, and their Derivatives

By Takeo SHIMA and Takashi AMIYA

(Received March 17, 1958)

It is well known that the pyrolysis of aconitine I ($C_{34}H_{47}O_{11}N$) at or above its melting point results in the internal loss of a molecule of acetic acid whereupon pyraconitine II ($C_{32}H_{43}O_9N$) is formed. Little is known, however, about the mode of elimination of acetic acid. Stern[1] mentioned that epoxide-formation occurred between the acetoxy group and an adjacent hydroxyl group or that a new ethylenic

1) R. H. F. Manske and H. L. Holmes, "The Alkaloids", Vol. IV, Academic Press Inc. New York. (1954), p. 292.

linkage was introduced by this pyrolysis. Recently on the ground of the observation of the infrared spectra Schneider[2] suggested that a new ethylenic linkage was introduced in the conjugated position to an inert ethylenic linkage initially present in compound I during pyrolysis of compound I by abstraction of a molecule of acetic acid between the acetoxy group and a hydrogen atom from a neighboring carbon atom. This mechanism was supported by Nath and Dasgupta[3,3a] although it had been previously denied by Edwards and Marion[4]. Attempts were made therefore to re-investigate pyrolytic reactions of compound I, oxonitine, and their derivatives by means of an examination of both ultraviolet and infrared spectra.

Thus, it was found that on pyrolysis of each of these alkaloids a new carbonyl group was formed by the splitting of a molecule of acetic acid between the acetoxy group and the hydroxyl group on a carbon atom near the acetoxy group.

Results were as follows:

Pyraconitine hydroperchlorate (III) ($C_{32}H_{43}O_9N \cdot HClO_4 \cdot H_2O$)[5,*]: infrared spectrum (nujol), >C=O and ester carbonyl 5.83 μ**; OH 3.01 μ: ultraviolet spectrum (methanol), λ_{max} 230 mμ, log ε 4.15; λ_{max} 275 mμ, log ε 3.03***.

Diacetyl pyraconitine (IV) ($C_{36}H_{47}O_{11}N \cdot C_2H_5OH$)[6,*]: infrared spectrum (nujol), >C=O 5.85 μ; ester carbonyl 5.76 μ; no-OH.

Pyroxonitine(V) ($C_{30}H_{37}O_{10}N$)[1]: infrared spectrum (nujol), lactam carbonyl 6.06 μ; >C=O and ester carbonyl 5.83 μ**; OH 3.01 μ: ultraviolet spectrum (methanol), λ_{max} 230 mμ, log ε 4.26; λ_{max} 275 mμ, log ε 3.03.

Diacetyl pyroxonitine(VI) ($C_{34}H_{41}O_{12}N \cdot C_2H_5OH \cdot H_2O$)[7,*]: infrared spectrum (nujol), lactam carbonyl 5.98 μ; >C=O 5.88 μ; ester carbonyl 5.80 μ; no-OH.

Pyraconine(VII) ($C_{25}H_{39}O_8N$)[8,****]: infrared spectrum (nujol), >C=O 5.88 μ; OH 2.94 μ: ultraviolet spectrum(methanol), λ_{max} 275 mμ, log ε 1.66.

Pyraconine hydrochloride(VIII) ($C_{25}H_{39}O_8N \cdot HCl \cdot 2.5H_2O$)*****,[8]: infrared spectrum (nujol), >C=O 5.94 μ; OH 2.94, 2.89, 2.87 μ: ultraviolet spectrum (methanol), λ_{max} 320 mμ, log ε 1.64.

Pyraconine hydroiodide(IX) ($C_{25}H_{39}O_8N \cdot HI \cdot H_2O$)[6]: infrared spectrum (nujol), >C=O 5.94 μ; OH 3.01, 2.88, 2.80 μ: ultraviolet spectrum (methanol), λ_{max} 220 mμ, log ε 4.11; λ_{max} 310 mμ, log ε 1.99.

Aconine(X) ($C_{25}H_{41}O_9N$)[8,****]: infrared spectrum (nujol), OH 2.88 μ: ultraviolet spectrum (methanol), no λ_{max} at wave lengths 210~350 mμ.

Aconine hydrochloride(XI) ($C_{25}H_{41}O_9N \cdot HCl \cdot 2H_2O$)[8,****]: infrared spectrum (nujol), H_2O 6.08 μ; OH 2.98 μ: ultraviolet spectrum (methanol), no λ_{max} at wave lengths 210~350 mμ.

Pyroxonine(XII) ($C_{23}H_{33}O_9N$)[1]: infrared spectrum (nujol), lactam carbonyl 6.08 μ, >C=O 5.87 μ; OH 3.01, 2.91 μ: ultraviolet spectrum (methanol), λ_{max} 305 mμ, log ε 1.64.

Oxonine(XIII) ($C_{23}H_{35}O_{10}N$)[1]: infrared spectrum (nujol), lactam carbonyl 6.02~6.07 μ; OH 2.9 μ.

Pyrodesmethanol aconitinone hydroperchlorate(XIV) ($C_{31}H_{37}O_8N \cdot HClO_4 \cdot H_2O$)[8]: ultraviolet spectrum (methanol), λ_{max} 233 mμ, log ε 4.39*.

Desmethanol aconitinone(XV) ($C_{33}H_{41}O_{10}N$)[8]: ultraviolet spectrum (methanol), λ_{max} 233 mμ, log ε 4.38[3a].

According to the above data there are marked differences between the absorption bands of compounds VII and VIII and those of compounds X and XI in the ultraviolet spectra and the infrared spectra. Also there was a marked difference in the infrared spectrum between the absorption bands of compound XII and those of compound XIII. Thus compounds VII, VIII and XII are believed to possess carbonyl groups newly formed by pyrolyses. Compounds IV and VI showed no bands at wave length 2.6~3.2 μ characteristic of hydroxyl group. This fact sug-

2) W. Schneider, *Ber.*, **89**, 768 (1956).
3) B. Nath, *J. Sci. Ind. Res., India*, **16, B**, 159 (1957).
3a) S. Dasgupta and B. Nath, *J. Ind. Chem. Soc.*, **34**, 204 (1957).
4) O. E. Edwards and L. Marion, *Can. J. Chem.*, **30**, 627 (1952).
5) H. Schulze and A. Liebner, *Arch. Pharm.*, **251**, 453 (1913).

* The infrared absorption spectra of these compounds were determined after drying in vacuo.
** This absorption band is broad.
*** The ultraviolet spectrum of compound III is nearly identical with that of pyraconitine.

6) H. Schulze and A. Liebner, *Arch. Pharm.*, **254**, 567 (1916).
7) K. Tamura, *Ann.*, **533**, 183 (1938).
8) T. A. Henry, "The Plant Alkaloids", J. & A. Churchill Ltd., London, (1949), p. 673.

**** Compounds VII, X and XI consume one mole each of periodic acid respectively. This fact suggests that the α-glycol of aconine X is not concerned in the pyrolytic reaction.
***** When aconine hydrochloride XI was heated at 180°C for 10 minutes pyraconine hydrochloride VIII was obtained. This compound VIII, which was crystallized from water, was identical with pyraconine hydrochloride which was prepared from pyraconitine by hydrolysis[1] (m. p. and analysis). *Anal.* Found: C, 54.01; H, 8.16. Calcd. for $C_{25}H_{45}O_{10.5}NCl$: C, 54.01; H, 8.18%.
* The ultraviolet spectrum of compound XIV was nearly identical with that of pyrodesmethanol aconitinone.

gests that a new carbonyl group was introduced by abstraction of a molecule of acetic acid between the acetoxy group and the hydroxyl group on a carbon atom near the acetoxy group. On the other hand there was no marked difference between the ultraviolet spectrum of compound III and that[9] of compound I at wave lengths 210~280 mμ. Hence, just as the former investigators[4] stated, no conjugated unsaturation results from pyrolysis. Reduction of compound VII with lithium aluminum hydride gave an amorphous base which the present workers named "pyraconiol". This base formed a hydroiodide which crystallized from water. Pyroconinol hydroiodide XVI ($C_{25}H_{41}O_3N \cdot HI \cdot 1.5H_2O$) showed m. p. 185°C (*Anal.* Found: C, 47.33; H, 7.23; H_2O, 4.25. Calc. for $C_{25}H_{45}O_{3.5}NI$: C, 47.20; H, 7.10; H_2O, 4.25%). The infrared absorption spectrum of compound XVI lacks the band corresponding to that (5.94 μ) of compound IX in the carbonyl region. Also the ultraviolet spectrum of compound XVI (λ_{max} 220 mμ, log ε 4.03) in methanol lacks a maximum corresponding to that (310 mμ) of compound IX in the carbonyl region. From the above data, it is suggested that the carbonyl group does not exist in compound XVI. The ultraviolet spectra of compound XIV and compound XV were rather similar at wave lengths 210~280 mμ. This fact suggests that the carbonyl group newly formed by pyrolysis in compound XIV is not conjugated to the α, β-unsaturated ketone which has been present in compound XV.

The authors are grateful to Professor Harusada Suginome, President of Hokkaido University, for his unfailing kindness in encouraging this work, and to Messrs. M. Yamaguchi and A. Fujino, Institute of Polytechnics, Osaka City University, for their kindness in the determination of the infrared spectra.

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9) E. Ochiai, T. Okamoto and S. Sakai, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **75**, 545 (1955).

SHORT COMMUNICATIONS

On the Extraction of Residual Lignin in the Unbleached Sulfite Pulp

By Koichiro Sato, Kiyo Ebisawa and Hiroshi Mikawa

(Received March 4, 1958)

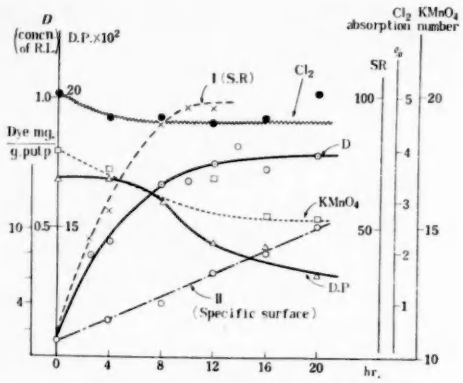
Generally lignin can not be removed completely by ordinary pulping process. In order to elucidate the bleaching mechanism, it is desirable to make clear the nature of the residual lignin (R.L.) in the unbleached pulp. Mainly because of the difficulties of separation of this lignin, almost nothing is known about it. As the reasons for this difficulty, one or several of the following facts will be considered in the case of sulpfite process. Residual lignin 1) is not sulfonated sufficiently, 2) is combined to carbohydrate firmly, 3) goes into solution with difficulty, because of morphological reasons of fiber, and 4) is condensed to other lignin unit during the digestion.

We have found that the resolution of residual lignin is effected with drastic beating in water, which causes fibrillation of the fiber and is expected to diminish morphological hindrance of the dissolution of R.L.

Commercial unbleached sulfite pulp (air dry, 540 g.) prepared from spruce (*Picea jezoensis*) was suspended in water (21 l) and beaten with Niagara-Type 1 to 1/2 pound Beater (Tappi-Standard T200m-45) for 20 hr.

Fig. 1 shows the course of treatment.

Curve I shows the increase of freeness. Freeness levels off at about SR 96 after 12 hr. no further increase being observed. Specific surface (curve II) measured with



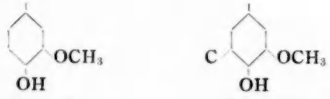
dye (Benzo Fast Scarlet 4BS) adsorption[1], increased linearly, and this shows that the fibrillation was progressing yet after beating 20 hr. On the other hand, the curves representing the permanganate number and the chlorine absorption of the beaten pulp have a slightly downward tendency.

The dissolution of R.L., measured by the ultraviolet absorption spectra of the filtrate of the beaten pulp which was diluted three times with water, reached maximum at 12 hr. After 8 hr., the D.P. of pulp began to decrease slowly. In this treatment the amount of the dissolved lignosulfonic acid does not exceed one-fifth of the total amount of R.L. Further dissolution of the remaining lignosulfonic acid in the beaten pulp is now under investigation.

The sulfonation degree of this lignin thus obtained is as low as that of the so-called "low-sulfonated lignosulfonic acid." Analytical data of R.L., low-sulfonated lignosulfonic acid (LSLA)[2] and ordinary lignosulfonic acid (L.S.A.)[3] are compared in the following table.

R.L.	$C_9H_{9.43}O_{3.90}(OCH_3)_{0.88}$
	$(SO_3Ba/2)_{0.27}S^{neut}_{0.335}$ $B^{excess}_{a_{0.014}}$
L.S.L.A.	$C_9H_{9.80}O_{3.76}(OCH_3)_{1.05}$
	$(SO_3Ba/2)_{0.23}S^{neut}_{0.03}$ $B^{excess}_{a_{0.028}}$
L.S.A.	$C_9H_{10.7}O_{3.2}(OCH_3)_{1.05}$
	$(SO_3Ba/2)_{0.51}S^{neut}_{0.08}$ $B^{excess}_{a_{0.04}}$

The amount of the total phenolic hydroxyl group of R.L. measured by the G.A.-Erdtman's method[4] is 0.17~0.21 per methoxyl, being the same with that of L.S.A. In the case of R.L. the phenolic hydroxyl group belonging to type I[5] is only 20% of the total, the remaining 80% being expected to be type II.



Type I Type II

Along with the dissolution of R.L., some amount of hemicellulose goes also into solution.

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1) E. F. Thode, J. W. Bedmesderfer and A. J. Chase: TAPPI **35** No. 8, 379 (1952); Sumikawa and Yoshino: unpublished data.
2) H. Mikawa, K. Sato, T. Takasaki and K. Ebisawa: unpublished data.
3) H. Mikawa, K. Sato, T. Takasaki and K. Ebisawa: This Bulletin **28** 653 (1955).
4) G. A. Erdtman: *Svensk Papperstidn* **56** (1953) 287.
5) H. Mikawa, K. Sato, T. Takasaki and K. Ebisawa: This Bulletin **29** 245 (1956).

Pure Quadrupole Spectrum of Trithiazyl Trichloride

By Hisao Negita and Ziro Hirano

(Received March 18, 1958)

So far we have studied pure quadrupole spectra of some heterocyclic compounds. In this connection, trithiazyl trichloride $(SNCl)_3$ was prepared[1] by chlorinating sulfur nitride $(SN)_4$. It is very unstable and reacts with moisture so easily that some precaution must be taken to preserve it. The spectrum due to ^{35}Cl was observed by the frequency-modulated super-regenerative spectrometer, and only one weak absorption line 29.842 megacycle/sec. was found at 285°K.

This result is evidently different from that of cyanuric chloride $(CNCl)_3$ which shows two adjacent lines[2], although trithiazyl trichloride might be benzene-like heterocyclic compound as well. It crystallizes in hexagonal prisms or needles, which should be closely related to the above fact. However, its crystal structure

1) A. Meuwsen, *Ber.*, **64**, 2311 (1931).
2) H. Negita and S. Satou, This Bulletin, **29**, 426 (1956).

has not yet been established.

On the other hand, it will be seen that the line situates in the neighborhood of those of thionyl chloride $SOCl_2$. This reminds us of the case of phosphonitrile chloride $(PNCl_2)_3$, where the lines are found at almost the same region as those of phosphorus oxychloride $POCl_3$. In the same way, those of cyanuric chloride are near to those of phosgene $COCl_2$. These results are summarized in Table I. When many lines are found in a compound, they are shown on an average for convenience.

TABLE I

COMPARISON OF ^{35}Cl RESONANCE ABSORPTION FREQUENCIES (ν) OF VARIOUS COMPOUNDS

Compd.	ν (Mc./sec.) at room temp.	Compd.	ν (Mc./sec.) at 77°K
$(SNCl)_3$	29.8	SO_2Cl_2	37.7[4]
		$SOCl_2$	31.9[5]
		PCl_5	32.4[6]
$(PNCl_2)_3$	27.8[2]	$POCl_3$	28.6[5]
		PCl_3	26.2[7]
$(CNCl)_3$	36.3[3]	CCl_4	40.6[7]
		$COCl_2$	35.7[7]

In this table, our data are concerned with the value at room temperature, and they should have about 1 megacycle/sec. added to them to compare with those of the compounds at 77°K. As seen from the table, there is a close relation between the valence state of the central atom, e.g., sulfur and the resonance frequency of the chlorine attached to it.

It would be difficult to explain the difference between the frequencies of sulfur and carbon compounds cited above in view of electronegativities of the composed atoms, because both sulfur and carbon atoms have the same negativity 2.5, according to Pauling. Of course, it is more difficult to interpret the slight frequency shifts between the ring compounds and the corresponding oxychlorides.

However, the frequency decrease of phosgene in comparison with cyanuric chloride might be attributed to its resonance structure $\dot{O}\equiv CCl\bar{C}l$ which may be deduced from the shorter distance 1.18A[8] between the carbon and oxygen than the normal double bond length 1.21A. The corresponding triple bond structure would hardly contribute anything to cyanuric chloride, and this may be the case also in both trithiazyl trichloride and thionyl chloride which is low pyramid structure[9].

The authors wish to express their thanks to Professor T. Ichikawa and Dr. H. Yamamura for their encouragement throughout this work.

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3) H. Negita, S. Satou. T. Yonezawa and K. Fukui, This Bulletin, **30**, 721 (1957).
4) P. J. Bray, *J. Chem. Phys.*, **23**, 703 (1955).
5) R. Livingston, *Phys. Rev.*, **82**, 289 (1951).
6) D. W. McCall and H. S. Guttowsky, *J. Chem. Phys.*, **21**, 1300 (1953).
7) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).
8) T. L. Cottrell and L. E. Sutton, *Quart. Rev.*, **2**, 260 (1948).
9) K. J. Palmer, *I. Am. Chem. Soc.*, **60**, 2360 (1938).

The Visible and Ultraviolet Absorption Spectra of Cellulose- and Amylose-Iodine Complexes

By Takehiro ABE

(Received April 16, 1958)

The structure of the amylose-iodine complex has been established, by Rundle and his co-workers[1], as a helical α-amylose chain in which the iodine molecules are arranged in a linear array, parallel to the helical axis. On the other hand, it has been described in a few books[2,3] that cellulose, structurally related to amylose, also gives a blue color on treatment with iodine. So, an attempt has been made, in the present work, to compare the cellulose-iodine complex with the amylose complex by means of their absorption spectra.

A solution of cellulose was obtained by dissolving a filter paper (the Toyo filter paper, No. 1 with a diameter of 12.5 cm.) into about 100 ml. of aqueous solution of commercial guaranteed zinc chloride. By adding a drop of solution of iodine and potassium iodide into this cellulose solution a deep blue color yields at once and numerous blue fibers precipitate. This blue color disappears at about 80°C by warming and re-appears by cooling.

1) R. E. Rundle and D. French, *J. Am. Chem. Soc.*, **65**, 1707 (1943); **69**, 1769 (1947).
2) Y. Kondo, "Experiments in Microchemistry of Cellulose Fibers", Bosekizashi, Osaka (1939), p. 5.
3) Y. Tsuzuki, "Simple Experiments in Organic Chemistry" Shokabo, Tokyo (1949), p. 58.

The visible absorption band of amylose-iodine complex has been found to shift toward the shorter wavelengths with increasing iodide concentration[4]. Thus, in the present measurement, a saturated iodine water was used to avoid an effect of iodide. The solution of cellulose-iodine complex to be measured was obtained after removing the blue fibers from the solution by a centrifuge.

α-Amylose was fractionated from an alkaline solution of potato starch as a complex with *n*-butanol[5]. The complex was crystallized three times from butanol. After washing it with ethanol it was dried by a vacuum pump for four hours and α-amylose was obtained. By adding a little iodine water into a solution of amylose and zinc chloride the sample of amylose-iodine complex was prepared. The absorption measurement was carried out with Hitachi Quartz Spectrophotometer Model EPU-2 at room temperature.

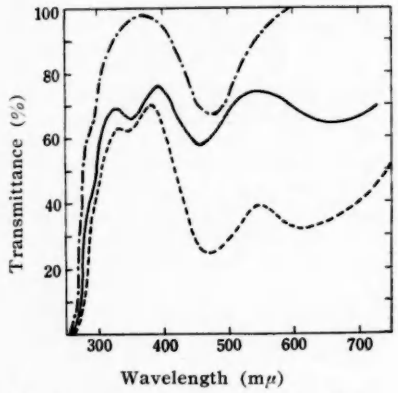

Fig. 1. Absorption spectra of cellulose-iodine complex (——), amylose-iodine complex (- - - -), and iodine in zinc chloride solution (—·—·—).

The results in Fig. 1 show that the absorption spectrum of cellulose-iodine complex in solution of zinc chloride is closely analogous to that of amylose-iodine. The absorption band at about 470 mμ seems to be attributed to iodine, because the spectrum of iodine in aqueous zinc chloride is observed at the same region. It is well known that a blue color of starch-iodine is decolorized by warming and is regenerated by cooling. As described above, the color of cellulose-iodine is found to behave like starch-iodine towards change in temperature. In the present experiments the cellulose-iodine complex is, thus, analogous to amylose-iodine. This fact leads to the suggestion that the cellulose-iodine complex is able to yield the blue color by the same mechanism as that by which the amylose-iodine does; in other words the iodine molecules may be arranged in the helical cellulose chain.

If a little of the iodine iodide solution is droped on a filter paper immersed in a solution of sodium hydroxide (of a concentration above several per cent.) for half an hour at room temperature and the paper is washed with water, a blue color can be seen distinctly on it. It has been found that the β-amylose is transformed to the helical α-amylose on treatment with a solution of sodium hydroxide[6]. It seems, therefore, possible that by sodium hydroxide cellulose is also transformed to a helical state giving a blue color with iodine.

The author is particularly indebted to Professor Y. Nomura for discussions and encouragement. The author also thanks Assistant Professor S. Maeda for use of the spectrophotometer.

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On the Radioactive Deposits of Thoron

By Hirotoshi Sano

(Received April 22, 1958)

Numerous reports have been published of the disintegration products of thoron or radon collected on a metal surface[1]. However, it seems to the present author that little information is available on the decay curve of such deposits collected on materials other than metals. To study

1) G. B. Cook and J. F. Duncan: "Modern Radiochemical Practice", Oxford, Clarendon Press, p. 14, (1952).

this problem, an experiment was performed in this laboratory. Copper plate, polyethylene film, and also the surface of water were used as collecting surface in this experiment. For not less than fifty hours, a collecting surface was exposed to a gas containing thoron, without application of electric field. The thoron was in equilibrium with thorium-X produced in crystalline thorium nitrate. As soon as the collecting surface was taken out from the gaseous medium, the radioactivity of the deposits was measured with a G–M counter. The geometry was kept as constant as possible for the counting of the activity of deposits on both copper plate and polyethylene film. Corrections were made for the coincidence loss on all the data obtained. It has been found that the amount of the radioactivity per unit area of collecting surface is roughly equal for different kinds of surface material, but the shape of the decay curve of the collected products depends on the kind of material. From the experimental results, the decay curves of the radioactive deposits were partly illustrated in Fig. 1. In Fig. 1, the decay curve A of the radioactive deposits collected on a copper plate constitutes almost a straight-line in semilogarithmic scale, showing the half-life of ThB (10.6 hr.). On the other hand, the decay curve B of the deposits collected on a polyethylene film shows some deviation from the straight-line at the initial stage of decay. Then it turned to a straight-line showing the half-life of ThB. For the measurement of the deposits collected on the surface of water, the water was evaporated up in a stainless steel dish and the radioactivity of the invisible residue was measured. The decay curve C obtained for the deposite on water has an intermediate shape between the cases of copper plate and polyethylene film. The total amount of the deposits collected on the surface of water is, however, smaller than that on the copper plate or polyethylene film because of the different surface area as well as the different geometry for the deposition. These results were always reproducible. The shapes of the decay curves indicate that there is some difference between the deposition velocity of ThB and ThC, and that the ratio of deposition velocity of ThC to ThB is greater for the collection on a copper plate than on a polyethylene film or the surface of water. To date, the phenomenon and the mechanism of the preferential deposition of some daughter disintegration products from thoron on different surface materials have not been described. Detailed results and probable explanation of the phenomenon will be reported elsewhere.

The author acknowledges with thanks the interest and encouragement of Dr. Nobufusa Saito, Professor of this laboratory.

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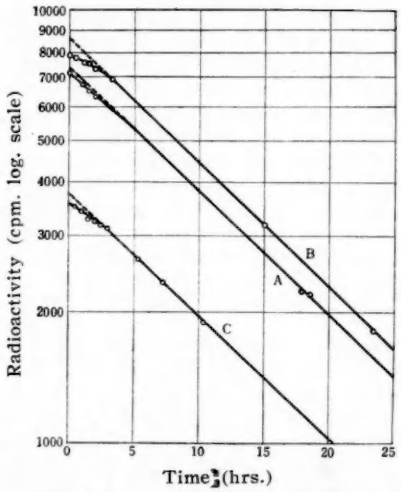

Fig. 1. Curve A: Copper plate.
Curve B: Polyethylene film.
Curve C: Surface of water.

The Polyaddition of Diphenylsilane to Difunctional Unsaturated Compounds

By Kuniharu Kojima

(Received April 25, 1958)

Since about 1947, it has been known that trichlorosilane adds to olefinic double bonds, under the influence of peroxide catalysts[1], azo catalysts[2], and platinum

1) L. H. Sommer et al., *J. Am. Chem. Soc.*, **69**, 188 (1947); **70**, 484 (1948); C. A. Burkhard et al., ibid., **69**, 2687 (1947); R. H. Krieble, U. S. Pat., 2,524,529. (1950).
2) R. V. Lipscomb, U. S. Pat., 2,570,462 (1951).

catalysts[3,4]. Methyldichlorosilane[5], phenylsilane[6], diphenylsilane[6] and phenylmethylsilane[6] also have been added to olefins, by the same method. Tribromosilane has been added to olefins, under the influence of ultraviolet light[7] and also at elevated temperatures[8].

Recently, platinum catalyzed additions of some chloro- and ethoxysilanes to a variety of vinyl[9], allyl[9] and methacrylic monomers[10] have been reported to give polymeric products in good yield under mild conditions.

I have now carried addition reaction between difunctional unsaturated compounds (divinyltetramethyldisiloxane or diallyl phthalate etc.) and diphenylsilane. In this case, the polyaddition products were obtained as resinous solid or viscous oily liquids.

Diallyl phthalate (4.92 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and platinum black catalyst (0.03 g.) were placed in a glass tube and it was sealed in a stream of nitrogen. The tube was heated at 110~120°C in an air oven for 50 hours. The reaction product was dissolved in benzene (100 c.c.) and reprecipitated with methanol (200 c.c.). The precipitate was separated and dried in a vacuum desiccator at 50°C for 7 days and analyzed for silicon and the molecular weight was determined by cryoscopic method in benzene.

Anal. Found: Si, 5.34. Calcd. for $C_{26}H_{26}O_4Si$: Si, 5.83 %. Mol. Wt., 2390. Yield, 76 %.

Divinyltetramethyldisiloxane (3.72 g., 0.02 mol.), diphenylsilane (3.68 g.) and platinum black (0.03 g.) were placed in a glass sealed tube. The tube was heated at 110~120°C in an air oven for 50 hours. The reaction product was dissolved in benzene and reprecipitated with methanol. The product was dried in a vacuum desiccator at 50°C, for 7 days, analyzed for silicon, and the molecular weight was determined.

Anal. Found: Si, 22.46. Calcd. for $C_{20}H_{30}OSi_3$: Si, 22.70 %. Mol. Wt., 2160. Yield, 78 %.

Further study is in progress.

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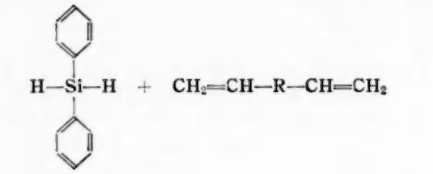

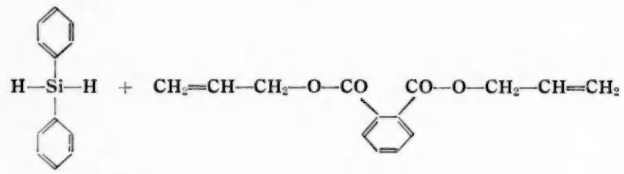

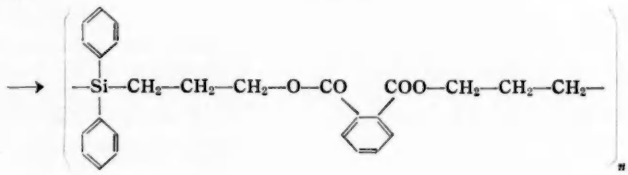

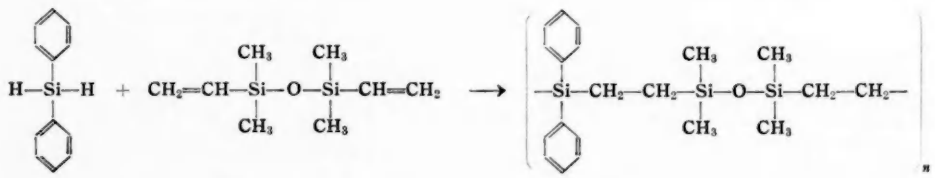

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The Isomerization of 2,4-Dinitrophenylhydrazones of α-Keto Acids

By Hirohiko KATSUKI, Koichiro SUMIZU, Tarumi MORIWAKI and Shozo TANAKA

(Received May, 20, 1958)

Most of 2, 4-dinitrophenylhydrazones of α-keto acids derived from monocarboxylic amino acids have been observed to give two spots on the paper chromatogram except dimethylpyruvic acid (DMPA) and methylethylpyruvic acid[1]. Because of the confirmation of the presence of *cis*- and *trans*-isomers in 2, 4-dinitrophenylhydrazones of pyruvic acid (PA), a representative of α-keto acid giving two spots on the paper chromatogram, we have ascribed these two spots to geometrical isomers of the hydrazones[2]. Furthermore we have recognized that DMPA, a representative of α-keto acid giving one spot on the paper chromatogram, gave only one isomer in some conditions on account of rapid isomerization velocity[3]. Since then in our laboratory the isomerization of these hydrazones had been studied and it was found that the directions of the isomerization were determined by the polarity of solvent.

Each component in the isomeric mixtures of the hydrazones of PA was determined by Hayashi's method[4] based on the fact that only the *cis*-form is extracted by ethyl acetate-ether mixture (3 : 1) from 0.1 % sodium carbonate solution containing 10 % sodium chloride. In less-polar solvent such as ethyl acetate, acetone or ether, the isomerization did not occur but in a polar solvent such as water or glacial acetic acid, the *cis*-form converted into the *trans*-form and a part of the hydrazone decomposed. But the inversion in the opposite direction was not observed. Both isomerization and decomposition were greatly accelerated by hydrogen ions. The rates of isomerization and decomposition of the *cis*-form in 0.3 N hydrochloric acid at 18°C for 5 hours, for example, were 30 % and 60 % respectively. On the other hand, in a less-polar solvent, hydrogen ions accerelated the interconversion in either direction and an equilibrium state was estabilshed, the composition of which being determined by the kind of solvent used, by the water content of the solvent and by temperature. For example, when standing in ethyl acetate saturated with 6 N hydrochloric acid for 30 min. at 18°C, the equilibrium mixture consisted of 46 % of the *cis*-form and 47 % of the *trans*-form. Seven per cent was proved to decompose.

In the case of the hydrazone of DMPA, the isomerization is so rapid that the equilibrium state is attained as soon as the isomer is dissolved in a solvent, and the simultaneous measurements of spectra of both isomers in the same solvent is impossible. For this reason the paper chromatogram gives only one spot. The α-isomer, m. p. 198°C (decomp.) is stable in anhydrous less-polar solvent, whereas the β-isomer, m. p. 188°C (decomp.) is stable in polar solvent. In absolute alcohol, the absorption maximum of the α-isomer in visible region lay at 365 mμ but with the increase of water content of the solvent it shifted to a longer wave length until it reached 380 mμ where the component consisted of β-isomer. The same results were obtained when formamide was used instead of water. That the rearrangement of the configuration of the hydrazone of DMPA occurred very easily was shown as follows: the freshly precipitated hydrazone in hydrochloric acid for the most part, consisted of the α-form but changed to the β-form within a few hours. Furthermore, when the sodium salt of the β-form was acidified with dilute hydrochloric acid precipitated free hydrazone at first was found to be the α-form. The structures of two isomers of the hydrazones of DMPA, at present, are not fully elucidated and will be discussed elsewhere.

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3) H. Katsuki, *J. Am. Chem. Soc.*, **77**, 4686 (1955).
4) I. Hayashi, private communication. Our sincere thanks are offered to him for his suggestion and continuous interest.

Adsorption Measurements during Surface Catalysis

By Kenzi TAMARU

(Received May 20, 1958)

It is one of the most fundamental problems in the field of surface catalysis to estimate the area of active part on catalyst surface. Since Taylor suggested his "active center theory" in 1925, many discussions have been presented from various view-points on the problem. Taylor emphasized that certain centers on the catalyst surface were responsible for most of the catalytic activity. These centers were tentatively identified as the corners and edges of the crystals in the surface. Other interpretations associated them with the existence of a number of different crystalline faces on the catalyst, each face having its own specific catalytic activity. The area of these active regions should accordingly be all extremes between the case in which all the atoms on the surface are active and that in which relatively few are active.

This short note is to emphasize a new approach to elucidate the mechanism of the catalytic reaction as well as the number of active atoms on the catalyst surface, measuring the adsorption during surface catalysis.

Recently it has been shown[1-4] that during the catalytic decomposition of germane (GeH_4) on germanium surface, which is a zero order reaction, the germanium surface is mostly saturated with chemisorbed hydrogen atoms. On the other hand it was also shown that the adsorption of hydrogen on germanium is an activated, reversible, dissociative and immobile adsorption, and also that if the chemisorbed hydrogen is supplied from the ambient hydrogen gas, the coverage of the surface in the adsorption equilibrium should be less than 0.6 under the experimental condition of the decomposition. From other data such as, for instance, obtained with deuterium and germanium deuteride, it was concluded that the desorption of chemisorbed hydrogen from the germanium surface is a rate-determining step of the overall decomposition reaction. All the evidence[1,3,5] seemed to indicate that the clean surface of germanium laid down by the decomposition of the hydride appeared to behave homogeneously energetic as to sites in the decomposition of the hydride, the major part of the germanium atoms on the surface participating in the catalysis.

It was thus suggested that the adsorption measurements during catalytic reaction would associate not only with the elucidation of the reaction mechanism, but also with the approximate estimation of active area of the catalyst surface, especially in the case of immobile adsorption.

When we study the kinetics of gas reaction on a solid catalyst, we elucidate the reaction mechanism, in most cases, on the basis of Langmuir-Hinshelwood, or sometimes, of Eley-Rideal mechanism, tacitly assuming that the elementary steps other than the rate-determining steps are all in equilibrium. The coverage of the surface to be guessed from the kinetics is that on the active part of the catalyst surface where the catalysis is actually taking place, and these coverages are not always the same with those derived from the adsorption equilibrium with the ambient gases, but are dependent upon the mechanism of the reaction, or the rate-determining step of the reaction, because of the free energy change accompanied by the reaction. This is the reason why the germanium surface is saturated with the chemisorbed hydrogen during the decomposition reaction, while the hydrogen adsorption equilibrium only covers less than sixty per-cent of the surface under the pressure.

If the adsorption on catalyst surface could be measured during reaction and the results were far from that on the active part which have been guessed from the kinetics, then we might consider that the active part on the catalyst surface which participates in the catalysis is a minor part of the surface. For instance, if a reaction is exactly zero order, it suggests that the active part of the catalyst surface is saturated with such things as reactants, products or intermediate compounds, the adsorption being independent of the ambient gas pressures. When the adsorption measurements during the reac-

1) K. Tamaru, M. Boudart and Hugh Taylor, *J. Phys. Chem.*, **59**, 801 (1955).
2) P. J. Fensham, K. Tamaru, M. Boudart and Hugh Taylor, ibid. 806 (1955).
3) K. Tamaru and M. Boudart, "Advances in Catalysis," Vol. IX Academic Press Inc., N.Y., p. 699 (1957).
4) K. Tamaru, *J. Phys. Chem.*, **61**, 647 (1957).
5) K. Tamaru, ibid., **60**, 612 (1956).

tion, however, would show the adsorption appreciably dependent upon the ambient gas pressure, it suggests that the active region is a minor part of the surface, and from the pressure-independent adsorption we could not only guess the area which participates in the catalysis, but also determine what actually saturates the active part, which suggests the rate-determining step of the overall reaction. On the other hand, if the adsorption is immobile and all the surface is saturated throughout the reaction, it suggests that all the surface is taking part in the catalysis, when the saturation does not result from the adsorption equilibrium of any of the ambient gases, as in the case of germane decomposition.

If the chemisorption of A in the catalytic reaction, $A+B \rightarrow C$, is rate-determining, the adsorption of A will not be observed during the reaction except the physical adsorption and the back-adsorption from C such as $C \rightleftarrows B(ads.)+A(ads.)$. The ammonia synthesis would be an example of this kind, as the chemisorption of nitrogen on the synthesis catalyst is generally accepted to be rate-determining.

Thus the new approach to measure the adsorption during catalytic reaction in addition to the separate measurements of each gas might enable us to attain a much better understanding of the mechanism of catalytic reaction as well as the nature of the catalyst surface. In most discussions of surfact catalysis it is tacitly assumed that the equilibrium case applies except the rate-determining step. We can also find with this new approach whether it is the case.

The adsorption measurements during reaction can be carried out in a closed circulating system in a similar way to those of the mixed adsorption. From the amount of the reactant introduced in the system and the pressure and the composition of the circulating gas, we can calculate the adsorbed amount of gases on the catalyst surface. The amount of catalyst is preferably large for accurate measurements and the adsorption should be measured under such conditions that the reaction takes place very slowly; otherwise the composition of the circulating gas will not be practically the same throughout the system and it might be affected by the heat of the reaction in the reactor.

The author wishes to express his gratitude to Sir Dean Hugh Taylor of Princeton University and Professor J. Horiuti and Professor T. Kwan of Hokkaido University for their valuable discussions and encouragement.

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Surface Areas of Sulfated Detergents

By Maresuke KASHIWAGI

(Received June 4, 1958)

The following report is concerned with surface films of some organic salts of lauryl sulfate. Apart from surface films of insoluble materials, relatively few data are available on the spread monolayers of soluble detergents. These soluble materials can not be spread under ordinary conditions, but by using a sufficiently high concentration of salts in the substrate, they can be expected to spread at the air-water interface. As for surface films of sodium lauryl sulfate (SLS), very useful studies[1-3] have been made since the early works of Bull[4] and Brady[5]. The present writer attemps here to investigate the spread surface films of morphorin, triethanolamine and pyridine salts of lauryl sulfate.

These three specimens are synthesized from lauryl alcohol and obviously they differ from one another only in end group attached to the same dodecyl sulfate portion of the molecule. It is therefore expected that the dodecyl sulfate portion with these heavy organic groups at the end would exhibit effects different from SLS, but it is found experimentally that they occupy the identical surface area with SLS.

Experimental

Materials.—A general synthetic method is as follows; thirty seven grams of lauryl alcohol distilled at 142~144°C/15 mmHg is sulfated in

1) B. A. Petheica, *Trans. Faraday Soc.*, **50**, 413 (1954).
2) J. T. Davis, *J. Colloid. Sci.*, **11**, 377 (1956).
3) G. Nilsson, *J. Phys. Chem.*, **61**, 1135 (1957).
4) H. B. Bull, *J. Am. Chem. Soc.*, **67**, 10 (1945).
5) A. P. Brady, *J. Colloid Sci.*, 4, 417 (1949).

hexane with 33 g. of pure chlorosulfonic acid at around 0°C over the period of 4 hours. After the completion of the reaction, the product is poured dropwise into 200 cc. of 10% aquous morpholin solution with stirring at the temperature below 5°C. The whole material is then shaken twice with petroleum ether to remove unreacted alcohol. The water portion is dried over the hot water bath and finally in a vacuum desiccator. The product is recrystalized repeatedly from ethylacetate or ethanol.

The chemical structure and nitrogen analysis are shown in Table I.

TABLE I
ANALYSIS OF LAURYL SULFATE

	N calcd.	Analysis found %
Morpholin	3.97	3.90
Triethanolamine	3.37	3.50
Pyridine	4.05	4.08

Measurements.—Surface pressure (F) is measured with a surface balance of Wilhelmy type. The detergent is spread from its *iso*-propanol (40% by volume)—water solution over the substrate containing 25% ammonium sulfate. After 10 minutes, the film is compressed to a desired area for the measurements.

Results.—Fig. 1 shows surface pressure changes of morpholin, triethanolamine and pyridine salt of lauryl sulfate on 25% ammonium sulfate at 18°C, respectively.

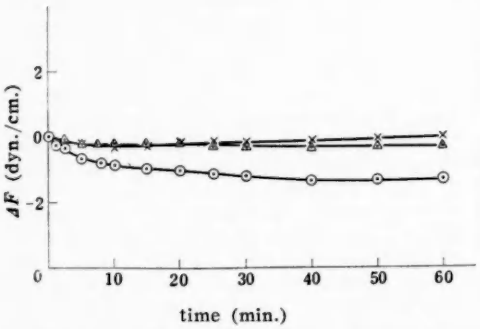

Fig. 1. Surface pressure changes with time (Substrate 25% $(NH_4)_2SO_4$)
Const. area

⊙	Morpholin	50.1 Å²/mol.
△	triethanolamine	50.7
×	pyridine	47.7

These $F-t$ curves indicate[6] that F does not decrease considerably and they make fairly stable monolayers inspite of heavy soluble organic group attached. Fig. 2 represents $F-A$ diagrams of these sulfated detergents on the same substrate. It appears that $F-A$ curves of these three specimens are approximately identical.

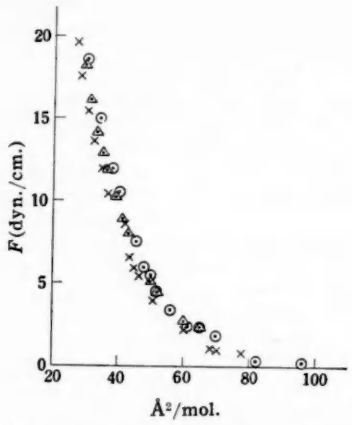

Fig. 2. Surface pressure-area diagrams (Substrate 25% $(NH_4)_2SO_4$)

⊙ Morpholin
△ triethanolamine
× pyridine

Discussion

It is known that spread and adsorbed monolayers of SLS are of the same character[1]. Although added salt condenses the monolayer as would be expected[7], Petheica has shown that all the monolayers obey the relation $F(A-A_0)=nkT$ where A_0 is a coarea term for an uncohering film, T the absolute temperature, k Boltzmann constant and n a constant.

The whole part of curves in Fig. 2 is slightly more expanded than SLS[1], but it obeys the above equation within graphical and experimental error. A_0 is thus calculated to be about 34 Å²/mol. between areas of 40 Å²/mol. and 70 Å²/mol. for all organic salts, and 40 Å²/mol., A_0 decreases to about 18 Å²/mol., which corresponds to the cross sectional area of hydrocarbon chain of the detergent molecule. It is interesting to note that these values of A_0 are in good agreement with surface areas of SLS calculated from the above equation of state or by other methods[1-3].

The writer wishes to express thanks to Professor Ryohei Matsuura of Kyushu University for his kind advice.

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6) M. Kashiwagi, This Bulletin, **30**, 176 (1958).

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Additions and Corrections

Volume 31, 1958

Dielectric Constant of Liquid Consisting of Anisotropic Molecules

By Masasi YASUMI, Hideo OKABAYASHI and Hitoshi KOMOOKA

The following tables are added. (Vol. 31, No. 4, p. 402).

TABLE I

DIELECTRIC CONSTANT OF BENZENE

(Å)		(10^{-25} cc.)
$a_1=7.1$	$a_2/a_1=1.00$	$\alpha_1=123.1$[1]
$a_2=7.1$		$\alpha_2=123.1$
$a_3=3.7$	$a_3/a_1=0.52$	$\alpha_3=63.5$

temp.(°C)	ε(Ob.)[2]	ε(L-L)[3]	ε(Cal.) (0.52)[4]
10	2.302	2.266	2.204
20	2.283	2.244	2.185
30	2.263	2.223	2.165
40	2.243	2.203	2.147
55	2.213	2.170	2.117
65	2.194	2.150	2.099

1) Stuart; loc. cit.
2) Observed values are refered in the following paper. R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).
3) Calculated value with Lorentz-Lorenz formula.
4) Calculated value with our formula assuming as the axial ratio 0.52.

TABLE II

DIELECTRIC CONSTANT OF CARBON DIOXIDE UNDER HIGH PRESSURE

(Å)		(10^{-25} cc.)
$a_1=5.3$	$a_2/a_1=0.52$	$\alpha_1=44.9$[1]
$a_2=3.0$		$\alpha_2=21.4$
$a_3=5.3$	$a_3/a_1=0.52$	$\alpha_3=21.4$

temp.=50°C

d_{amagat}	ε(Ob.)[2]	ε(L-L)	ε(Cal.) (0.6)
24.28	1.02486	1.02433	1.02436
61.20	1.06343	1.06216	1.06202
116.87	1.12444	1.1208	1.1205
231.23	1.25991	1.2487	1.2477
350.40	1.41189	1.3943	1.3898
470.70	1.57801	1.5546	1.5456
549.90	1.69318	1.6684	1.6562
595.89	1.76244	1.7380	1.7232

1) Stuart; loc. cit.
2) Michels and Kleerekoper; Physica, **6**, 586 (1939).

TABLE III

DIELECTRIC CONSTANT OF CARBON DISULFIDE

(Å)			(10^{-25} cc.)
$a_1=6.8$	$a_2/a_1=0.54$		$\alpha_1=151.4$[1]
$a_2=3.7$			$\alpha_2=55.4$
$a_3=3.7$	$a_3/a_1=0.54$		$\alpha_3=55.4$

temp.(°C)	ε(Ob.) (Z.I.)[2]	ε(Ob.) (Fè)[3]	ε(Ob.) (G)[4]	n^2(L.W.)[5]	ε(L-L)	ε(Cal.) (0.5)
40		2.603			2.671	2.545
25		2.625			2.716	2.584
20	2.626	2.632	2.635	2.650	2.732	2.600
15			2.648			
10	2.657	2.644		2.673	2.765	2.625
0	2.688	2.658	2.661	2.699	2.799	2.655
− 20	2.740	2.686	2.739	2.752	2.861	2.708
− 40	2.792		2.794	2.806	2.928	2.762
− 60	2.839		2.850	2.859	2.993	2.819
− 80	2.885		2.904	2.914	3.063	2.876
−100	2.954		2.961	2.969	3.137	2.935
−110	2.988			2.996	3.172	2.966

1) Stuart; loc. cit.
2) A. A. Zuehke and L. R. Ingersoll; *J. Opt. Soc. Amer.*, **27**, 314 (1937).
3) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).
4) M. R. Guillerin; *Compt. rend*, **206**, 1001 (1938).
5) N. Lyon and F. Wolfram; *Ann. d. Physik*, **63**, 739 (1920).

TABLE IV

DIELECTRIC CONSTANT OF CARBON DISULFIDE UNDER HIGH PRESSURE

temp.=30°C

Press.(Atm.)	ε(Ob.)[1]	ε(L-L)	ε(Cal.)(0.5)
1	2.61	2.67	2.56
500	2.74	2.79	2.66
1000	2.82	2.88	2.73
2000	2.94	3.03	2.85
4000	3.11	3.27	3.05
6000	3.23	3.45	3.19
8000	3.33	3.60	3.29
12000	3.52	3.87	3.52

1) W. E. Danforth; *Phys. Rev.*, **38**, 1224 (1931).

TABLE V

DIELECTRIC CONSTANT OF METHYL FLUORIDE UNDER HIGH PRESSURE

(Å)		(10^{-25} cc.)*
$a_1=4.7$	$a_2/a_1=0.85$	$\alpha_1=31.6$[1]
$a_2=4.0$		$\alpha_2=23.2$
$a_3=4.0$	$a_3/a_1=0.85$	$\alpha_3=23.2$

$\mu_0=1.79$ D (Stark effect)[2]

temp.=50°C

Press.(Int. Atm.)	ε(Ob.)[3]	ε(Cal.)(1.7)[4]
21.706	1.218	1.207
29.919	1.333	1.316
41.373	1.551	1.517
49.400	1.783	1.729
55.683	2.067	1.982
60.819	2.496	2.38
63.630	3.001	2.84
65.468	3.811	3.63
66.190	4.210	4.08
67.287	4.726	4.62
69.052	5.214	5.15
71.724	5.659	5.68
74.993	5.992	6.06
81.402	6.422	6.54

1) C. G. Le Fèvre and R. J. W. Le Fèvre; loc. cit.

2) S. N. Ghosh, R. Trambarulo and W. Gordy; *J. Chem. Phys.*, **21**, 308 (1953).

3) H. G. David, S. D. Hamann and J. F. Pearse; *J. Chem. Phys.*, **20**, 969 (1952).

4) Calculated value with our formula assuming as the axial ratio 1.7.

* In the literature of C. G. Le Fèvre and R. J. W. Le Fèvre, the authors assume that $P_E+P_A=9$ cc. and $P_E=6.6$ cc.. However, we assume that $P_A=0$, $P_E=9$ cc.. Using this value we calculate the values of the components of polarizability.

TABLE VI

DIELECTRIC CONSTANT OF METHYL CHLORIDE

(Å)		(10^{-25} cc.)
$a_1=5.6$	$a_2/a_1=0.71$	$\alpha_1=54.2$[1]
$a_2=4.0$		$\alpha_2=41.4$
$a_3=4.0$	$a_3/a_1=0.71$	$\alpha_3=41.4$

$\mu_0=1.87$ D (Stark effect)[2]

temp. (°C)	ε(Ob.)[3] (M.L.)	ε(Ob.) (Fevre)[4]	ε(Cal.) (0.71)	ε(Cal.) (0.75)
−20	12.61	12.6	11.90	12.22
−30	13.26	13.22	12.61	12.91
−40	14.02	14.07	13.38	13.75
−50	14.88	15.00	14.21	14.66
−60	15.84	15.95	15.19	15.64
−70	16.88	16.92	16.23	16.75
−80	18.02		17.44	18.03
−90	19.27		18.76	19.45

1) Stuart; loc. cit.

2) R. G. Shulman, C. H. Towres and B. P. Dailey; *Phys. Rev.*, **78**, 145 (1950).

3) S. C. Morgan and H. H. Lowry; *J. Phys. Chem.*, **34**, 3285 (1930).

4) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).

TABLE VII

DIELECTRIC CONSTANT OF METHYL BROMIDE

(Å)		(10^{-25} cc.)
$a_1=5.9$	$a_2/a_1=0.68$	$\alpha_1=68.5$[1]
$a_2=4.0$		$\alpha_2=49.0$
$a_3=4.0$	$a_3/a_1=0.68$	$\alpha_3=49.0$

$\mu_0=1.80$ D (Stark effect)[2]

temp. (°C)	ε(Ob.) (M.L.)[3]	ε(Cal.) (0.68)	ε(Cal.) (0.6)
0	9.97	10.50	9.67
−10	10.42	11.05	10.17
−20	10.91	11.69	10.73
−30	11.43	12.39	11.32
−40	12.00	13.13	11.99
−50	12.63	13.95	12.73
−60	13.32	14.85	13.50
−70	14.07	15.86	14.39
−80	14.96	16.96	15.35
−90	16.02	18.18	16.41
−100	17.4	19.61	17.66

1) Stuart; loc. cit.

2) R. G. Schulman, C. H. Townes and B. P. Dailey; *Phys. Rev.*, **78**, 145 (1950).

3) S. O. Morgan and H. H. Lowry; *J. Phys. Chem.*, **34**, 3285 (1930).

TABLE VIII

DIELECTRIC CONSTANT OF METHYL IODIDE

(Å)		(10^{-25} c.c.)
$a_1=6.3$	$a_2/a_1=0.64$	$\alpha_1=87.2$[1]
$a_2=4.0$		$\alpha_2=65.7$
$a_3=4.0$	$a_3/a_1=0.64$	$\alpha_3=65.7$

$\mu_0=1.65$ D (Stark effect)[2]

temp. (°C)	ε(Ob.) (M.L.)[3]	ε(Cal.) (0.60)	ε(Cal.) (0.45)
40	6.50	7.33	6.35

30	6.75	7.65	6.60
20	7.00	8.00	6.86
10	7.26	8.36	7.14
0	7.53	8.76	7.45
−10	7.81	9.17	7.77
−20	8.13	9.64	8.12
−30	8.48	10.14	8.50
−40	8.87	10.68	8.91
−50	9.28	11.29	9.37
−60	9.74	11.91	9.85
−70	10.33	12.63	10.39

1) Le Fèvre; loc. cit.
2) R. G. Shulman, C. H. Townes and B. P. Dailey; *Phys. Rev.*, **78**, 145 (1950).
3) S. O. Morgan and H. H. Lowry; *J. Phys. Chem.*, **34**, 3285 (1930).

TABLE IX

DIELECTRIC CONSTANT OF ACETONITRILE

(Å)		(10⁻²⁵ cc.)
$a_1=6.2$	$a_2/a_1=0.64$	$\alpha_1=54.3$[1]
$a_2=4.0$		$\alpha_2=37.0$
$a_3=4.0$	$a_3/a_1=0.64$	$\alpha_3=37.0$

$\mu_0=3.92$ D (Stark effect)[2]

temp. (°C)	ε(Ob.)[3] (U.N)	ε(Ob.) (G.P.)[4]	ε(Ob.) (T)	ε(Cal.) (0.7)
15	38.3			37.4
20	37.5		37.45	36.4
25	36.7			35.4
82		26.2		26.3

1) Le Fèvre; loc. cit.
2) S. N. Ghosh, R. Trambarulo and W. Gardy: *J. Chem. Phys.*, **21**, 308 (1953).
3) H. Ulich and W. Nespital; *Z. Physik. Chem.*, **B16**, 221 (1932).
4) F. V. Grimm and W. A. Patrick; *J. Am. Chem. Soc.*, **45**, 2794 (1923).
5) J. Timmermans, A. M. Piette and R. Phillipe; *Bull. Soc. Chim. Belges*, **64**, 5 (1955).

TABLE X

DIELECTRIC CONSTANT OF TERT-BUTYL CHLORIDE

(Å)		(10⁻²⁵ cc.)
$a_1=6.2$	$a_2/a_1=1.11$	$\alpha_1=109.2$[1]
$a_2=6.9$		$\alpha_2=92.6$
$a_3=6.9$	$a_3/a_1=1.11$	$\alpha_3=92.6$

$\mu_0=2.13$ D (Vapour)[2]

temp. (°C)	ε(Ob.) (S)[3]	ε(Cal.) (1.33)
−20	12.2	12.32
−10	11.5	11.58
0	10.95	10.90
10	10.4	10.29
15		10.00
20		9.73
30	9.37	9.19

1) Le Fèvre; loc. cit.
2) B. H. Wismall and C. P. Smyth; *J. Chem. Phys.*, **9**, 356 (1941).
3) W. O. Baker and C. P. Smyth; *J. Am. Chem. Soc.*, **61**, 2798 (1939).

TABLE XI

DIELECTRIC CONSTANT OF CHLOROFORM

(Å)		(10⁻²⁵ cc.)
$a_1=4.6$	$a_2/a_1=1.54$	$\alpha_1=66.8$[1]
$a_2=7.1$		$\alpha_2=90.1$
$a_3=7.1$	$a_3/a_1=1.54$	$\alpha_3=90.1$

$\mu_0=1.05$ D (Vapour)[2]

temp. (°C)	ε(Ob.) (M.L.)[3]	ε(Ob.) (F)[4]	ε(Ob.) (C)[5]	ε(Cal.) (1.54)	ε(Cal.) (1.82)
60	4.12			3.80	4.03
50	4.29	4.31		3.95	4.19
40	4.47	4.47		4.09	4.35
30	4.65	4.64		4.24	4.53
20	4.84	4.81	4.785	4.40	4.71
10	5.02	5.00		4.57	4.90
0	5.22	5.19	5.172	4.74	5.10
−10	5.43	5.40		4.94	5.34
−20	5.65	5.51	5.601	5.15	5.58
−30	5.89			5.38	5.85
−40	6.16		6.095	5.62	6.14
−50	6.45			5.91	6.47
−60	6.79		6.772	6.21	6.83

1) Stuart; loc. cit.
2) S. C. Sircar; *Indian J. Phys.*, **3**, 197.
3) S. C. Morgan and H. H. Lowry; *J. Phys. Chem.*, **34**, 3285 (1930).
4) R. J. W. D. Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).
5) I. E. Coop; *Trans. Faraday Soc.*, **33**, 583 (1937).

TABLE XII

DIELECTRIC CONSTANT OF NITROMETHANE

(Å)		(10⁻²⁵ cc.)
$a_1=5.5$	$a_2/a_1=0.94$	$\alpha_1=51.8$[1]
$a_2=5.2$		$\alpha_2=71.7$
$a_3=4.0$	$a_3/a_1=0.73$	$\alpha_3=18.3$

$\mu_0=3.46$ D (Stark effect)[2]

temp. (°C)	ε(Ob.) (B.M.)[3]	ε(Ob.) (T.P.P.)[4]	ε(Cal.)[5]
10	39.1		31.3
20		38.57	
30	35.9		28.3
50	32.9		25.5
70	30.1		23.1
90	27.6		20.9

1) Le Fèvre; loc. cit.
2) E. Tannenbaum, R. J. Myers and W. D. Gwinn; *J. Chem. Phys.*, **25**, 42 (1956).
3) F. Buckley and A. A. Maryott; Jour. of Research of National Bureau of Standards, **53**, 229 (1954).
4) J. Timmermans, A. M. Piette and R. Phillipe; *Bull. soc. chim. Belges*, **64**, 5 (1955).
5) For asymmetric top molecules the value of dielectric constant is calculated with our formula using as the value of the axial ratio, the value determined with the molecular model.

TABLE XV
DIELECTRIC CONSTANT OF DIETHYL ETHER

(Å) $(10^{-25}$ cc.)

$a_1=4.9$[1] $a_2/a_1=1.80$ $\alpha_1=78.7$[2]

$a_2=8.8$ $\alpha_2=112.6$

$a_3=4.0$ $a_3/a_1=0.82$ $\alpha_3=70.7$

$\mu_0=1.17$ D (Vapour)[3]

temp. (°C)	ε(Ob.) (S)[4]	ε(Ob.) (F)[5]	ε(Ob.) (C)[6]	ε(Ob.) (T)[7]	ε(Ob.) (L.L)[8]	ε(Cal.) (E)[9]	ε(Cal.) (O.S.)[10]
−116	10.42					6.43	9.21
−101	9.05					5.87	8.28
− 80			7.541			5.24	7.18
− 75	7.25					5.11	6.93
− 60	6.55		6.545			4.79	6.37
− 40		5.91	5.791			4.36	5.67
− 30	5.45	5.60				4.18	5.38
− 20		5.325	5.180			4.01	5.09
− 10	4.96	5.066				3.86	4.86
0	4.75	4.803	4.706			3.71	4.64
10		4.575				3.58	4.43
15		4.480				3.52	4.33
18				4.360		3.48	4.28
20	4.29	4.376	4.300			3.46	4.23
25		4.265				3.40	4.13
30		4.152				3.34	4.04
40				3.966		3.22	3.88
60				3.652		3.02	3.57
80				3.375		2.84	3.29
100				3.122		2.65	3.02
120				2.890		2.47	2.78
128					2.716	2.41	2.67
140				2.658		2.30	2.54
143					2.557	2.28	2.50
158					2.392	2.15	2.33
160				2.408		2.13	2.30
168					2.270	2.05	2.20
180				2.124	2.081	1.905	2.02
190				1.885	1.878	1.738	1.814
193				1.533	1.798	1.648	1.702

1) This structure corresponds to the planar zig-zag form.
2) Stuart; loc. cit.
3) L. G. Groves and S. Sudgen; *J. Chem. Soc.*, 1779 (1935).
4) S. A. McNeight and C. P. Smyth; *J. Am. Chem. Soc.*, **58**, 1718 (1936).
5) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).
6) I. E. Coop; *Trans. Faraday Soc.*, **33**, 583 (1937).
7) Karl Tangl; *Ann. d. Physik*; **10**, 748 (1903).
8) N. Litrinoff and W. Litrinoff; *Z. Physik*; **57**, 134 (1929).
9) The value calculated with our formula assuming the value of the axial ratio the value corresponding to the planar zig-zag form.
10) Molecular model is assumed to be the oblate spheroid whose axial ratio is 0.5 : 1 : 1.

TABLE XIII

DIELECTRIC CONSTANT OF METHYLENE CHLORIDE

(Å)		(10^{-25} cc.)
$a_1=4.4$	$a_2/a_1=1.50$	$\alpha_1=59.6$[1]
$a_2=6.6$		$\alpha_2=84.7$
$a_3=4.0$	$a_3/a_1=0.91$	$\alpha_3=50.2$

$\mu_0=1.62$ D (Stark effect)[2]

temp.(°C)	ε(Ob.) (M.L.)[3]	ε(Cal.)
40	8.29	7.57
30	8.71	7.93
20	9.14	8.31
10	9.58	8.72
0	10.02	9.19
−10	10.51	9.62
−20	11.00	10.22
−30	11.56	10.82
−40	12.14	11.46
−50	12.77	12.17
−60	13.49	12.94
−70	14.23	13.78
−80	15.05	14.74
−90	15.97	15.79
−100	16.98	16.94

1) Stuart; loc. cit.
2) R. J. Myers and W. D. Gwinn; *J. Chem. Phys.*, **20**, 1420 (1952.)
3) S. O. Margan and H. H. Lowry; *J. Phys. Chem.*, **34**, 3285 (1930).

TABLE XIV

DIELECTRIC CONSTANT OF DIMETHYL ETHER

(Å)		(10^{-25} cc.)
$a_1=4.3$	$a_2/a_1=1.47$	$\alpha_1=48.6$[1]
$a_2=6.3$		$\alpha_2=63.0$
$a_3=4.0$	$a_3/a_1=0.93$	$\alpha_3=43.1$

$\mu_0=1.30$ D (Vapour)[2]

temp.(°K)	ε(Ob.)[3]	ε(Cal.)
298	5.02	4.45
318	4.54	4.01
338	4.07	3.62
358	3.59	3.22
378	3.12	2.79
398	2.37	2.15

1) Stuart; loc. cit.
2) L. G. Groves and S. Sudgen; *J. Chem. Soc.*, 1779 (1937). K. L. Ramaswamy; *Proc. Indian Acad. Sci.*, **A4**, 108 (1936).
3) J. Marsden and O. Maass; *Can. J. Research*; **B13**, 296 (1935).

TABLE XVI

DIELECTRIC CONSTANT OF *n*-PROPYL ETHER

(Å)		(10^{-25} cc.)
$a_1=$ 4.9[1]	$a_2/a_1=2.41$	$\alpha_1=117.0$[2]
$a_2=11.8$		$\alpha_2=137.0$
$a_3=$ 4.0	$a_3/a_1=0.82$	$\alpha_3=122.0$

$\mu_0=1.18$ D (Vapour)[3]

temp.(°C)	ε(Ob.)[4]	ε(Cal.)
26	3.39	3.36

1) These values correspond to the planar zig-zag form.
2) Stuart; loc. cit.
3) G. A. Barclay and R. J. W. Le Fèvre; *J. Chem. Soc.*, 1643 (1952).
4) Pyle; *Phys. Rev.*, **38**, 1057 (1931).

TABLE XVII

DIELECTRIC CONSTANT OF PARALDEHYDE

(Å)		(10^{-25} cc.)
$a_1=4.0$	$a_2/a_1=2.05$	$\alpha_1=116.2$[1]
$a_2=8.2$		$\alpha_2=129.2$
$a_3=8.2$	$a_3/a_1=2.05$	$\alpha_3=129.2$

$\mu_0=1.43$ D (Vapour)[2]

temp.(°C)	ε(Ob.)[3]	ε(Cal.)[4]
20	14.70	11.62
40	12.25	10.23
60	10.30	9.04
80	8.70	8.03
100	7.46	7.14
120	6.42	6.38

1) Le Fèvre; loc. cit.
2) R. J. W. Le Fèvre, J. W. Mulley and B. M. Smyth; *J. Chem. Soc.*, 291 (1950).
3) R. C. Miller and C. P. Smyth; *J. Phys. Chem.*, **60**, 1354 (1956).
4) We assume that the polarizability effective for the dielectric constant is $(P_A+P_E)/P_E$ times the value estimated by Le Fèvre.

TABLE XVIII

DIELECTRIC CONSTANT OF ACETONE

(Å)		(10^{-25} cc.)
$a_1=5.4$	$a_2/a_1=1.24$	$\alpha_1=69.6$[1]
$a_2=6.7$		$\alpha_2=72.2$
$a_3=4.0$	$a_3/a_1=0.74$	$\alpha_3=48.2$

$\mu_0=2.87$ D[2] (Vapour)

temp.(°C)	ε(Ob.) (C.)[3]	ε(Ob.) (E.)[4]	ε(Cal.)
−80	34.5		33.3
−59	31.31		28.6
−40	28.42		25.2
−20	25.91		22.3
0	23.65	21.58	19.8
10		20.49	18.6
15		19.99	18.1
20	21.54	19.54	17.6
25		19.10	17.2
30		18.68	16.6
40	19.38	17.82	15.8
50		17.00	14.9

1) Stuart assumes that the value of the dipole moment is 2.7 D. But we recalculate the values of components of polarizability assuming that $\mu_0=2.87$ D.
2) K. L. Ramaswamy; *Proc. Indian Acad. Sci.*, **A4**, 108 (1936).
3) R. H. Cole; *J. Chem. Phys.*, **9**, 251 (1941).
4) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).

TABLE XIX

DIELECTRIC CONSTANT OF METHYL-ETHYL KETONE

(Å)		(10^{-25} cc.)
$a_1=5.4$[1]	$a_2/a_1=1.50$	$\alpha_1=85.5$[2]
$a_2=8.1$		$\alpha_2=98.3$
$a_3=4.0$	$a_3/a_1=0.74$	$\alpha_3=60.2$

$\mu_0=2.87$ D[3]

temp. (°C)	ε(Ob.) (C.)[4]	ε(Ob.) (F.)[5]	ε(Cal.)
0	20.30		16.8
5		20.35	16.3
10		19.83	15.9
15		19.33	15.5
20	18.51	18.85	15.1
25		18.41	14.7
40	16.80		13.6
60	15.29		12.3
80	13.89		11.2

1) This assumed structure is the planar zig-zag form.
2) Stuart; loc. cit.
3) We assume that the value of the dipole moment has the same value as that of acetone.
4) R. H. Cole; *J. Chem. Phys.*, **9**, 251 (1941).
5) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).

TABLE XX

DIELECTRIC CONSTANT OF DIETHYL KETONE

(Å)		(10^{-25} cc.)
$a_1=5.4$[1]	$a_2/a_1=1.67$	$\alpha_1=100.1$[2]
$a_2=9.0$		$\alpha_2=126.4$
$a_3=4.0$	$a_3/a_1=0.74$	$\alpha_3=71.5$

$\mu_0=2.87$ D[3]

temp. (°C)	ε(Ob.) (C.)[4]	ε(Cal.)
−40	19.77	18.5
−20	19.37	16.4
0	18.90	14.7
20	17.00	13.2
40	15.31	11.9
60	15.83	10.9
80	12.52	9.91
100	11.49	9.08

1) The structure corresponds to the planar zig-zag form.
2) Stuart; loc. cit.
3) We assume that the value of the dipole moment has the same as for acetone.
4) R. H. Cole; *J. Chem. Phys.*, **9**, 251 (1941).

TABLE XXI

DIELECTRIC CONSTANT OF TOLUENE

(Å)		(10^{-25} cc.)
$a_1=8.5$	$a_2/a_1=0.76$	$\alpha_1=156.4$[1]
$a_2=6.5$		$\alpha_2=136.6$
$a_3=4.0$	$a_3/a_1=0.47$	$\alpha_3=74.8$

$\mu_0=0.37$ D (Vapour)[2]

temp. (°C)	ε(Ob.)[3]	ε(Cal.)
−50	2.5889	2.563
−33	2.5336	2.504
−15	2.4785	2.450
0	2.4350	2.406
10	2.4065	2.377
25	2.3661	2.337
35	2.3421	2.312
45	2.3196	2.286
60	2.2846	2.252
80	2.2449	2.205
100	2.2061	2.159
110	2.1901	2.139

1) Stuart; loc. cit.
2) J. W. Baker and L. G. Groves; *J. Chem. Soc.*, 1144 (1939).
3) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).

TABLE XXII

DIELECTRIC CONSTANT OF *o*-XYLENE

(Å)		(10^{-25} cc.)
$a_1=7.8$	$a_2/a_1=0.92$	$\alpha_1=163.9$[1]
$a_2=7.1$		$\alpha_2=135.2$
$a_3=4.0$	$a_3/a_1=0.51$	$\alpha_3=107.5$

$\mu_0=0.62$ D (Vapour)[2]

temp. (°C)	ε(Ob.)[3]	ε(Cal.)
−20	2.701	2.768
0	2.648	2.679
20	2.594	2.599
40	2.541	2.526
60	2.488	2.459
80	2.434	2.399
100	2.381	2.341
120	2.328	2.287
130	2.302	2.258

1) Le Fèvre; loc. cit.
2) E. C. Hurdis, and C. P. Smyth; *J. Am. Chem. Soc.*, **64**, 2212 (1942).
3) L. M. Heil; *Phys. Rev.*, **39**, 666 (1932).

TABLE XXIII

DIELECTRIC CONSTANT OF CHLOROBENZENE

(Å)		(10^{-25} cc.)
$a_1=8.5$	$a_2/a_1=0.76$	$\alpha_1=155.1$[1]
$a_2=6.5$		$\alpha_2=138.2$
$a_3=3.7$	$a_3/a_1=0.44$	$\alpha_3=74.2$

$\mu_0=1.70$ D[2] (Vapour)

temp. (°C)	ε(Ob.) (F.)[3]	ε(Ob.) (S.)[4]	ε(Ob.) (C.)[5]	ε(Cal.)
−50		7.28		7.88
−40			6.872	7.54
−30		6.76		7.20
−20			6.401	6.92
−10		6.26		6.64
0			5.982	6.40
10		5.82		6.15
20			5.605	5.95
21	5.670			5.93

25	5.612		5.84
30		5.46	5.75
40	5.372		5.55
48			5.41
50		5.15	5.38
70	4.886	4.89	5.04
80	4.768		4.90
96.2	4.521		4.66
100		4.52	4.61
106	4.435		4.53
115	4.314		4.42
130		4.17	4.24
131	4.144		4.23

1) Stuart assumes that the dipole moment has the value of 1.60 D. However we recalculate the polarizability value assuming μ_0= 1.70 D.
2) L. G. Groves and S. Sudgen; *J. Chem. Soc.*, 1094 (1934).
3) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).
4) C. P. Smyth and S. O. Morgan; *J. Am. Chem. Soc.*, **50**, 1547 (1928).
5) I. E. Coop; *Trans. Faraday Soc.*, **33**, 583 (1937).

TABLE XXIV

DIELECTRIC CONSTANT OF BROMOBENZENE

(Å)		(10^{-25} cc.)
a_1=8.8	a_2/a_1=0.74	α_1=168.4[1]
a_2=6.5		α_2=121.3
a_3=3.9	a_3/a_1=0.44	α_3 =95.6

μ_0=1.64 D[2] (Vapour)

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
1	5.74	6.37
25	5.39	5.84
40	5.18	5.58
55	4.96	53.0

1) Le Fèvre; loc. cit.
2) R. J. W. Le Fèvre and Narayana Rao; *Australian J. Chem.*, **8**, 140 (1955).
3) W. A. Hestone, E. T. Hennelly and C. P. Smyth; *J. Am. Chem. Soc.*, **72**, 2071 (1950).

TABLE XXV

DIELECTRIC CONSTANT OF FLUOROBENZENE

(Å)		(10^{-25} cc.)
a_1=7.6	a_2/a_1=0.85	α_1=112.6[1]
a_2=6.5		α_2=110.6
a_3=3.7	a_3/a_1=0.49	α_3= 71.1

μ_0=1.57 D[2] (Vapour)

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
25	5.42	5.18
60	4.76	4.58

1) Le Fèvre; loc. cit.
2) K. B. McAlpine and C. P. Smyth; *J. Chem. Phys.*, **3**, 55 (1935).
3) A. A. Maryott and E. R. Smyth; "Table of Dielectric Constants of Pure Liquid." NBS Circular 514 (1951).

TABLE XXVI

DIELECTRIC CONSTANT OF IODOBENZENE

(Å)		(10^{-25} cc.)
a_1=9.2	a_2/a_1=0.71	α_1=198.4[1]
a_2=6.5		α_2=140.7
a_3=4.3	a_3/a_1=0.47	α_3=113.6

μ_0=1.70 D[2] (Vapour)

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
20	4.625	5.48

1) Le Fèvre; loc. cit.
2) E. C. Hurdis and C. P. Smyth; *J. Am. Chem. Soc.*, **64**, 2212 (1942). R. J. W. Le Fèvre and Narayana Rao; *Australian J. Chem.*, **8**, 140 (1955).
3) A. Audsley and Goss; *J. Chem. Soc.*, 497 (1942).

TABLE XXVII

DIELECTRIC CONSTANT OF *o*-DICHLOROBENZENE

(Å)		(10^{-25} cc.)
a_1=7.7	a_2/a_1=0.92	α_1=176.8[1]
a_2=7.1		α_2=158.5
a_3=4.3	a_3/a_1=0.55	α_3= 89.7

μ_0=2.50 D[2] (Vapour)

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
0	11.130	13.0
25	9.930	11.6
50	8.900	10.4

1) Stuart assumes that the value of the dipole moment is 2.25 D. But we recalculate the values of the components of polarizability assuming that μ_0=2.50 D.
2) E. M. Moore and M. E. Hobbs; *J. Am. Chem. Soc.*, **71**, 411 (1949). E. C. Hurdis and C. P. Smyth; *J. Am. Chem. Soc.*, **64**, 2212 (1942).
3) C. P. Smyth and S. P. Morgan; *J. Am. Chem. Soc.*, **50**, 411 (1928).

TABLE XXVIII

DIELECTRIC CONSTANT OF *m*-DICHLOROBENZENE

(Å)		(10^{-25} cc.)
a_1=7.1	a_2/a_1=1.28	α_1=158.2[1]
a_2=9.1		α_2=178.4
a_3=3.7	a_3/a_1=0.52	α_3= 90.4

μ_0=1.72 D (Vapour)[2]

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
0	5.403	6.97
25	5.039	6.34
50	4.703	5.82

1) Stuart assumes that the value of dipole moment is 1.48 D. But we recalculate the values of the components of polarizability assuming that μ_0=1.72 D.
2) L. G. Groves and S. Sudgen; *J. Chem. Soc.*, 1782 (1937).
3) C. P. Smyth and S. O. Morgan; *J. Am. Chem. Soc.*, **50**, 1547 (1928).

TABLE XXIX

DIELECTRIC CONSTANT OF BENZONITRILE

(Å)		(10^{-25} cc.)
$a_1=9.2$	$a_2/a_1=0.71$	$\alpha_1=163.8$[1]
$a_2=6.5$		$\alpha_2=121.1$
$a_3=3.7$	$a_3/a_1=0.41$	$\alpha_3=84.9$

$\mu_0=4.14$ D (Stark effect)[2]

temp.(°C)	ε(Ob.)(M.)[3]	ε(Ob.)(T.)[4]	ε(Cal.)
0	27.6		26.7
18	25.85		24.6
20		25.58	24.2
25	25.2		23.7
30			23.2
40	24.0		22.2
50			21.3
50.3	23.28		21.2
60	22.7		20.3
70	22.1		19.5

1) Le Fèvre; loc. cit.
2) Lide; *J. Chem. Phys.*, **22**, 1577 (1954).
3) A. R. Martin; *Trans. Faraday Soc.*, **33**, 191 (1938).
4) J. Timmermans; A. M. Piette and R. Phillippe; *Bull. soc. chim. Belges*, **64**, 5 (1955).

TABLE XXX

DIELECTRIC CONSTANT OF NITROBENZENE

(Å)		(10^{-25} cc.)
$a_1=8.5$	$a_2/a_1=0.76$	$\alpha_1=171.6$[5]
$a_2=6.5$		$\alpha_2=141.9$
$a_3=3.7$	$a_3/a_1=0.44$	$\alpha_3=74.1$

$\mu_0=4.19$ D (Vapour)[3]

temp.(°C)	ε(Ob.)[4]	ε(Cal.)
10	37.85	28.0
25	34.89	26.1
30	33.97	25.5
40	32.26	24.4
50		23.4
60	29.08	22.4
70		21.4
90	24.88	19.8
110	22.68	18.3
130	20.79	16.9
150	19.27	15.8
170	18.15	14.6
200	15.95	13.1
211	15.61	12.7

1) The structure corresponds to the planar form.
2) Stuart assumes that the value of the dipole moment is 3.92 D. However we recalculate the value of polarizability assuming $\mu_0=4.19$ D.
3) K. B. McAlpine and C. P. Smyth; *J. Chem. Phys.*, **55**, (1935).
4) R. J. W. Le Fèvre; *Trans. Faraday Soc.*, **34**, 1127 (1938).

TABLE XXXI

DIELECTRIC CONSTANT OF PYRIDINE

(Å)		(10^{-25} cc.)
$a_1=6.6$	$a_2/a_1=0.98$	$\alpha_1=108.4$[1]
$a_2=6.5$		$\alpha_2=118.8$
$a_3=3.7$	$a_3/a_1=0.56$	$\alpha_3=57.8$

$\mu_0=2.15$ D[2] (Stark effect)

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
1	14.65	12.0
20	13.55	11.0
40	12.45	10.1
60	11.44	9.26

1) Stuart; loc. cit.
2) B. B. De More, W. S. Wilcox and J. H. Goldstein; *J. Chem. Phys.*, **22**, 876 (1954).
3) Russel, Holland and C. P. Smyth; *J. Phys. Chem.*, **59**, 1088 (1955).

TABLE XXXII

DIELECTRIC CONSTANT OF QUINOLINE

(Å)		(10^{-25} cc.)
$a_1=7.1$	$a_2/a_1=1.25$	$\alpha_1=165$[1]
$a_2=8.9$		$\alpha_2=224$
$a_3=3.7$	$a_3/a_2=0.52$	$\alpha_3=79.5$

$\mu_0=2.29$ D[2] (Vapour)

temp.(°C)	ε(Ob.)[3]	ε(Cal.)
1	9.70	10.19
20	9.03	9.44
40	8.40	8.77
90	7.81	8.19

1) Le Fèvre; loc. cit.
2) A. D. Buckinghas, J. Y. H. Chan, H. C. Freeman, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao and J. Tardif; *J. Chem. Soc.*, 1405 (1956).
3) Russell, Holland and C. P. Smyth; *J. Phys. Chem.*, **59**, (1955).